Synthesis, Characterization and Catalytic Study of (9-Anthryl)(iminophosphorano)methanide and (9-Anthryl)(thiophosphinoyl)methanide Metal Complexes

HO, Ming Gong

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Thesis/ Assessment Committee

Prof. Thomas C. W. MAK (Chair)

Prof. Kevin W.-P. LEUNG (Thesis Supervisor)

Prof. T. NGAI (Committee Member)

Prof. Cameron JONES (External Examiner)

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Ming Gong HO
Department of Chemistry
The Chinese University of Hong Kong

Abstract

The work presented in the thesis is focused on three parts: (i) the synthesis and structural characterization of (9-anthryl)(iminophosphorano)methanide group 14 metal complexes, and (ii) the synthesis and structural characterization of (9-anthryl)(iminophosphorano)methanide early transition metal complexes, and (iii) the synthesis and structural characterization of (9-anthryl)(thiophosphinoyl)methanide metal complexes.

Chapter 1 describes the development of group 14 metal complexes derived from (9-anthryl)(iminophosphorano)methane [$CH_2(Pr^i_2P{=}NSiMe_3)(Anth)$] (Anth = 9-anthryl) (**42**). Group 14 metal complexes, [$M\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}Cl$] [M = Ge (**44**), Sn (**45**)] and [$Sn\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2$] (**46**) have been prepared by metathesis reaction of an intermediate lithium complex, [$Li\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}$] (**43**), with the corresponding group 14 metal chlorides. Compounds **44-46** have been structurally characterized by spectroscopic methods and X-ray crystallography.

Chapter 2 describes the synthesis and structural characterization of (9-anthryl)(iminophosphorano)methanide early transition metal complexes. The metal complexes, [$M\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2Cl_2$] [M = Zr (**57**), Hf (**58**)] have been prepared by metathesis reaction of intermediate lithium complex **43** with the

corresponding group 4 metal chlorides. Compounds **57** and **58** have been structurally characterized by spectroscopic methods and X-ray crystallography. The catalytic activities of compounds **57** and **58** towards ethylene polymerization have been investigated.

Chapter 3 describes the synthesis and characterization of (9-anthryl)(thiophosphinoyl)methanide lithium complex, $[Li(THF)_2\{CH(Pr^i_2P{=}S)(Anth)\}]$ (**93**). The germanium complex, $[Ge(GeCl)\{CH(Pr^i_2P{=}S)(Anth)\}_2Cl{\cdot}2C_6H_5CH_3]$ (**94**), has been prepared by the metathesis reaction of **93** with $GeCl_2{\cdot}$dioxane. X-ray structure analysis of **94** showed that it contains both Ge(II) and Ge(IV) centers within the same molecule. Also, metathesis reaction of **93** with $ZrCl_4$ in diethyl ether affords the zirconium complex $[Zr\{CH(Pr^i_2P{=}S)(Anth)\}_2Cl_2(THF){\cdot}THF]$ (**95**). Compounds **93-95** have been structurally characterized by spectroscopic methods and X-ray crystallography. The catalytic activity of compound **95** towards ethylene polymerization has also been investigated.

摘要

本論文論述的內容主要包括以下三部分：（i）從 9-芴基膦亞胺配體衍生出的低價態第十四主族金屬復合物的合成及其結構研究，（ii）從 9-芴基膦亞胺配體衍生出的第四族過渡金屬復合物的合成及其結構研究，（iii）從新型 9-芴基膦亞硫配體衍生出的金屬復合物的合成及其結構研究。

第一章介紹從 9-芴基膦亞胺配體衍生出的低價態第十四主族金屬復合物的合成及其結構研究。從膦亞胺配體 [$CH_2(Pr^i_2P{=}NSiMe_3)(Anth)$] (**42**) 出發，中間物鋰綜合體[$Li\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}$] (**43**) 被合成出來。中間物 **43** 與低價態第十四族金屬氯化物進行交換反應，分別產生化合物 [$Ge\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}Cl$] (**44**), [$Sn\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}Cl$] (**45**) 及 [$Sn\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2$] (**46**)。

第二章介紹從 9-芴基膦亞胺配體衍生出的第四族過渡金屬復合物的合成及其結構研究。中間物 **43** 與第四族過渡金屬氯化物進行類似的交換反應，分別產生化合物 [$Zr\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2Cl_2$] (**57**) 及 [$Hf\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2Cl_2$] (**58**)。第四族金屬復合物 **57** 及 **58** 對乙烯聚合反應的催化活性也被考究。

第三章介紹從新型 9-芴基膦亞硫配體衍生出的金屬復合物的合成及其結構研究。從膦亞硫配體 [$CH_2(Pr^i_2P{=}S)(Anth)$] (**92**) 出發，鋰化合物

$[Li(THF)_2\{CH(Pr^i_2P=S)(Anth)\}]$ (**93**) 被合成出來。鋰化合物 **93** 與二氯化鍺及四氯化鋯進行交換反應，分別產生 $[Ge(GeCl)\{CH(Pr^i_2P=S)(Anth)\}_2Cl\cdot 2C_6H_5CH_3]$ (**94**) 及 $[Zr\{CH(Pr^i_2P=S)(Anth)\}_2Cl_2(THF)\cdot THF]$ (**95**)。第四族金屬復合物 **95** 對乙烯聚合反應的催化活性也被考究。

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List of Compounds Synthesized

Abbreviation

Anth	anthryl
Bu^n	butyl
Bu^t	*tert*-butyl
Calcd.	calculated
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	doublet (spectral)
dd	doublet of doublet (spectral)
Et_2O	diethyl ether
Hz	hertz
J	coupling constant (spectral)
Ln	lanthanide (Sc, Y, La, Ce-Lu)
m	multiplet (spectral)
M	parent peak (mass spectrum)
Me	methyl
Mp.	melting point
MHz	megahertz

MS	mass spectroscopy
m/z	mass to charge ratio (mass spectroscopy)
NMR	nuclear magnetic resonance
Ph	phenyl
Pr^i	isopropyl
Py	pyridyl
r.t.	room temperature
s	singlet (spectral)
t	triplet (spectral)
THF	tetrahydrofuran

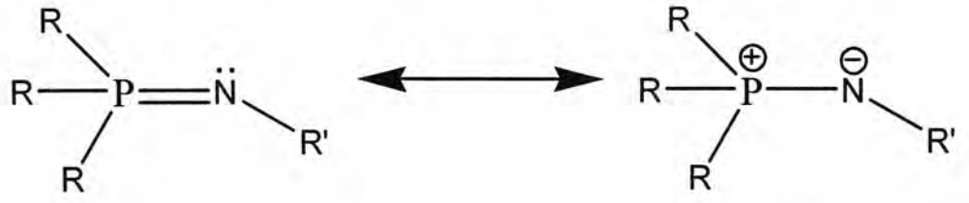
CHAPTER 1

SYNTHESIS AND CHARACTERIZATION OF (9-ANTHRYL)(IMINOPHOSPHORANO)METHANIDE GROUP 14 METAL COMPLEXES

1.1 Introduction

1.1.1 A General Review of Phosphoranoimine Ligands

Phosphoranoimines were first prepared by Staudinger and Meyer in 1919.[1] Since then, the chemistry of phosphoranoimines has been of great interest and studied comprehensively. They have a general structure $R_3P{=}NR'$ with four-coordinate phosphorus and incorporating a formal phosphorus-nitrogen double bond which is polar in nature.[2] Two resonance structures are possible for phosphoranoimines, which are the double-bonded ylide (**I**) and the dipolar ylidic form (**II**) (**Figure 1.1**).[3]



I **II**

Figure 1.1

Phosphoranoimines can be prepared readily in two major routes. The first one is the Staudinger reaction, in which tertiary phosphines react with organoazides with the elimination of molecular nitrogen (**Scheme 1.1**).[1] The second one is the Kirsanov

reaction, in which tertiary phosphino halides react with primary amines to give phosphoranoimines (**Scheme 1.2**).[2]

$$R_3P + R'N_3 \longrightarrow [R_3PN_3NR'] \xrightarrow{-N_2} R_3P{=}NR'$$

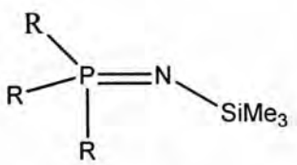
Scheme 1.1

$$R_3PX_2 + 3\ R'NH_2 \longrightarrow R_3P{=}NR' + 2\ R'NH_3X$$

X = Cl, Br

Scheme 1.2

Phosphoranoimines have been used as monodentate or bidentate ligands in synthesizing metal complexes in coordination and organometallic chemistry.[3,4] Some examples (**1-3**) are shown in **Figure 1.2**.[5-9] Furthermore, phosphoranomines with a side-arm containing other chelating groups such as nitrogen-substituted or phosphorus-substituted to become tridentate or tetradentate ligands can enhance the stability of the metal complexes formed. The ligands which have this feature are called heterodifunctional ligands, and selected examples (**4-9**) are shown in **Figure 1.3**.[5, 10-14]



R = Pr^i, Ph, Cy

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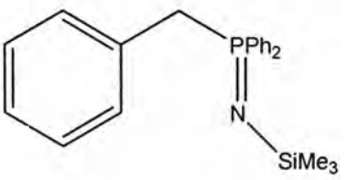

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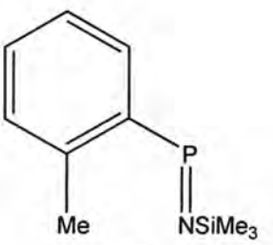

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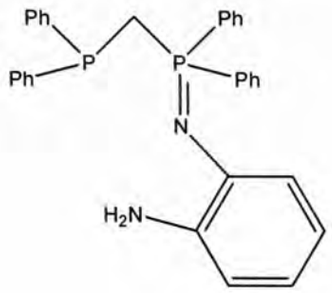
Figure 1.2



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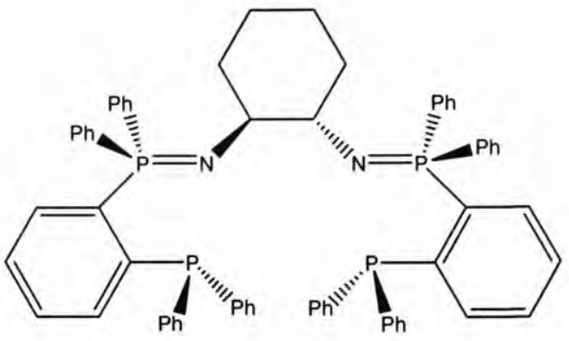

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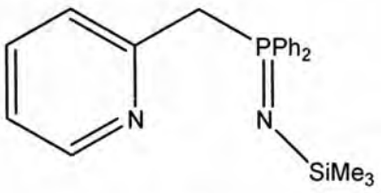

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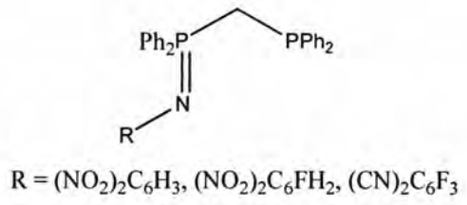

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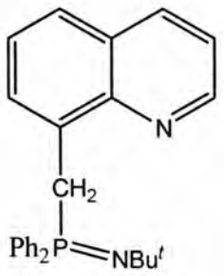

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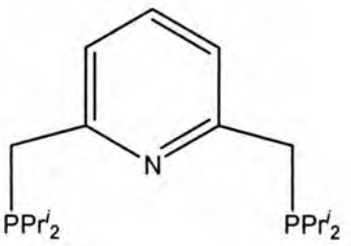

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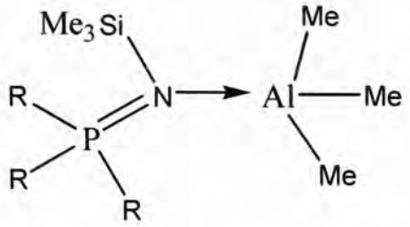
Figure 1.3

The lone pair electrons of the nitrogen atom of phosphoranoimines can be used to form various main group and transition metal complexes. In this case, the specific phosphoranoimines behave as neutral ligands. Examples of such metal complexes include $[(R_3P{=}NSiMe_3)AlMe_3]$ (R = Pr^i, Ph Cy) (**10**)[6], $[t\text{-}Bu_2(2\text{-}C_6H_4Ph)P{=}NTiCl_3]$ (**11**)[15], $[\{PhP(2\text{-}Me_2CHOC_6H_4)\}\{THF\}TiCl_3]$ (**12**)[16], $[(Ph_3P{=}NSiMe_3)CuCl]$ (**13**)[17] and $[M\{2\text{-}CH_2Py\}PR_2{=}NSiMe_3]Cl_2]$ (**14**)[18] are shown in **Figure 1.4**.



R = Pr^i, Ph, Cy

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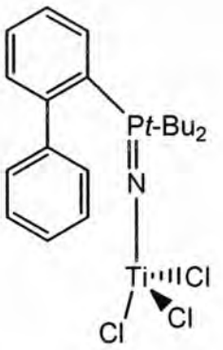

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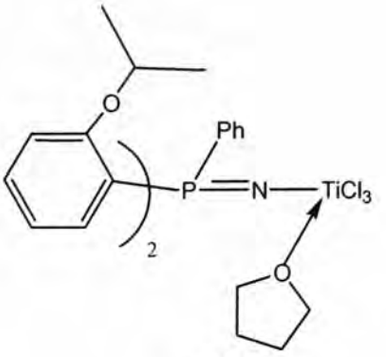

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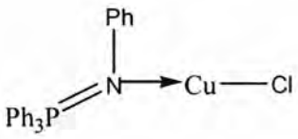

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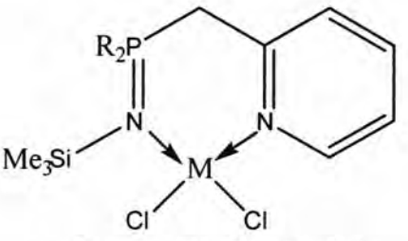

M = Fe, Co; R = Ph, Pr^i

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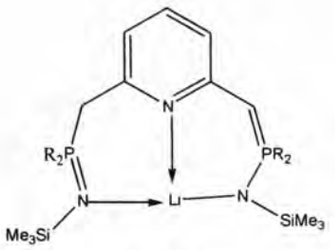
Figure 1.4

In *P*-alkyl phosphoranoimines, the methylene proton at the α-C positions can be deprotonated to give alkali or alkaline-earth metal complexes. The metal center is typically bonded to the anionic ligand via a bidentate *C,N*-chelating or *N,N'*-chelating fashion. For examples, alkali metal complexes, [Li{2,6-($Me_3SiN{=}PPr^i_2CH$)($Me_3SiN{=}PPr^i_2CH_2$)C_5H_3N}] (**15**)[19], [{[$(THF)_2Li(Me_3SiN{=}PPr^i_2CH)$]$_2$-2,3-$C_4H_4N_2$}] (**16**)[20], and [M{$HC(Ph_2P{=}NSiMe_3)_2$-κ*N*,κ*N*'}$(THF)_2$] [M = Na (**17**); K (**18**)][8]; and alkaline earth metal complex, $[HC(Ph_2P{=}NSiMe_3)_2MgI(THF)]$ (**19**)[21] have been reported and are shown in **Figure 1.5**.



R = Ph, Pr^i

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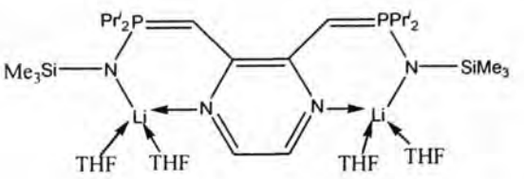

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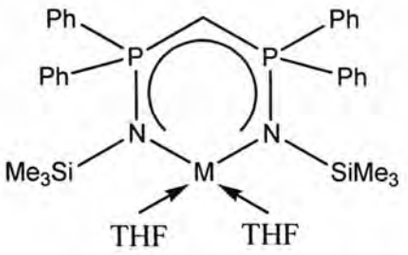

M = Na (**17**); K (**18**)

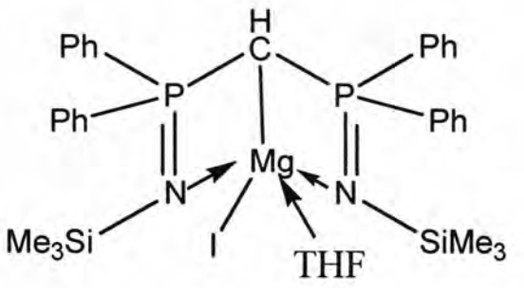

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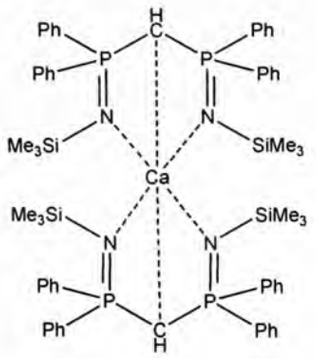
Figure 1.5

The alkali-metal salts of phosphoranoimines can undergo metathesis reaction with corresponding main-group, transition and lanthanide metal chlorides to afford various types of metal complexes. For example, main group metal complexes, $[M\{HC(Ph_2P{=}NSiMe_3)_2\}_2]$ [M = Ca (**20**)[22]; Ba (**21**)[23]]; transition metal complexes, $[ZnEt\{2\text{-}(3,5\text{-}Me_2C_3HN_2)\text{-}6\text{-}\{N(Ph)P(Ph)_2{=}CH\}C_5H_3N\}]$ (**22**)[24], $[\{HC(Ph_2PNC_6H_2Me_3\text{-}2,4,6)_2\}MN(SiMe_3)_2]$ [M = Mn (**23**), Fe (**24**), Co (**25**)][25]; and lanthanide metal complexes, $[\{HC(Ph_2P{=}NSiMe_3)_2\}LnCl_2]_2]$ [Ln = Y (**26**), Sm (**27**), Dy (**28**), Er (**29**), Yb (**30**), Lu (**31**)][26] have been reported and are shown in **Figure 1.6**.



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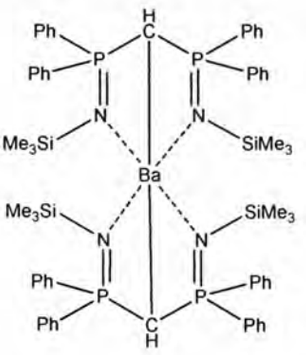

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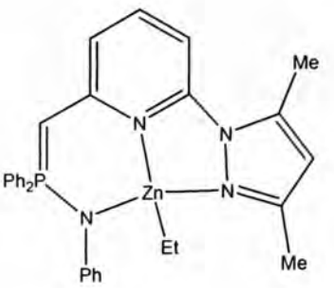

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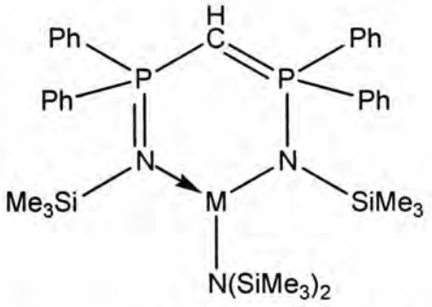
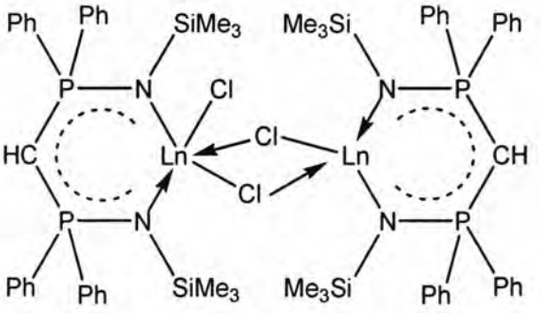


M = Mn (**23**), Fe (**24**), Co (**25**)



Ln = Y (**26**), Sm (**27**), Dy (**28**), Er (**29**), Yb (**30**), Lu (**31**)

Figure 1.6

Cavell and coworkers have successfully synthesized a dilithium complex, $[\{Li_2\{C(Ph_2P{=}NSiMe_3)_2\}\}_2]$ (**32**), which has an unusual cluster structure as shown in **Figure 1.7**.[27]

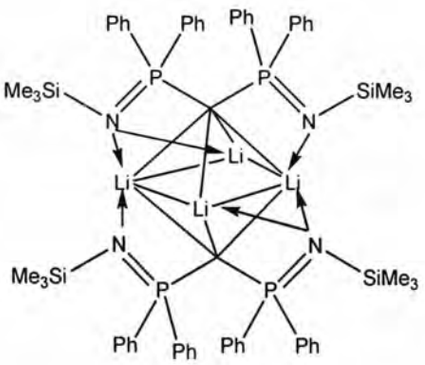


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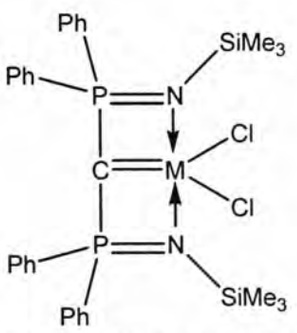
Figure 1.7

This dianionic lithium complex **32** undergoes metathesis reaction with main-group and transition metal chlorides to afford carbene-like complexes which have been reviewed.[28] For example, $[MCl_2\{C(Ph_2P{=}NSiMe_3)_2\}]$ [M = Ti (**33**), Zr (**34**)][29] and $[\{Cr\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}\}_2]$ (**35**)[30] have been reported and they are shown in **Figure 1.8**. After that, calcium and barium carbenes, $[\{(Me_3SiN{=}PPh_2)_2CCa\}_2]$ (**36**)[22] and $[\{(Me_3SiN{=}PPh_2)_2CBa{\cdot}THF\}_2]$ (**37**)[23] with similar structures as that of **35,** have also been reported by Harder and coworkers (**Figure 1.9**).



M = Ti (**33**), Zr (**34**)

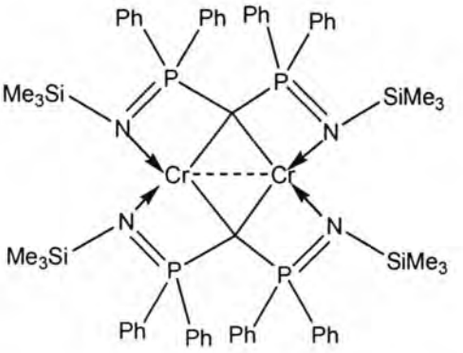


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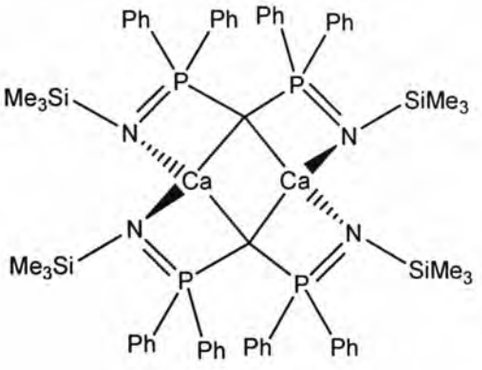
Figure 1.8



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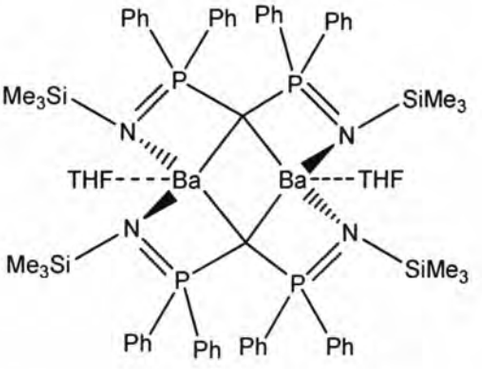
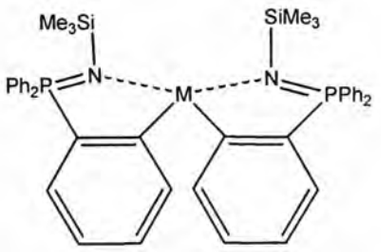


37

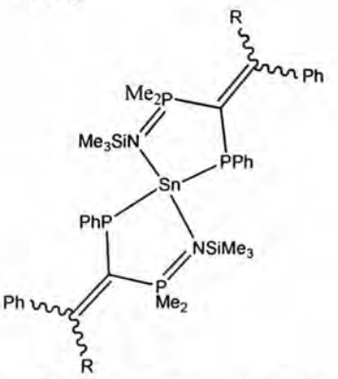
Figure 1.9

1.1.2 A General Review of Group 14 Metal Complexes Containing Phosphoranoimine Ligands

Lappert and coworkers have reported the novel synthesis of low-valent group 14 metal alkyls more than 30 years ago.[31] Much efforts have been made in exploring the chemistry of other low-valent group 14 element compounds with the general formula of R_2M: (R = alkyl or amide) afterwards.[32-35] However, these compounds are generally unstable and prone to undergo polymerization. To solve this problem, bulky and functionalized ligands are usually employed to stabilize the thermodynamically stable compounds formed. In this case, phosphoranoimido ligands bearing the bulky *N*- or *P*-alkylated substituents would be suitable for the synthesis group 14 metal complexes. For examples, $[M(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ [M = Sn (**38**), Pb (**39**)][36], $[Sn\{P(Ph)C\{=C(H)Ph\}P(Me)_2=NSiMe_3\}_2]$ (**40**)[37] and $[Sn\{P(Ph)C\{=C(Ph)SiMe_2Bu^t\}P(Me)_2=NSiMe_3\}_2]$ (**41**)[37] have been reported (**Figure 1.10**).



M = Sn (**38**), Pb (**39**)

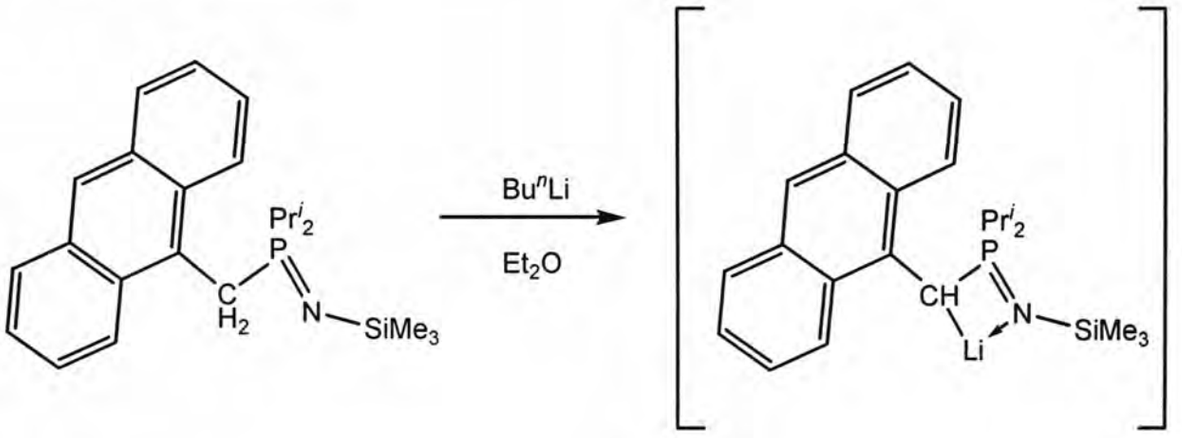


R = H (**40**), $SiMe_2Bu^t$ (**41**)

Figure 1.10

1.2 Objectives

The objective of this thesis is to prepare phosphoranoimine metal complexes using (9-anthryl)(iminophosphorano)methane (**42**) as the ligand backbone (**Figure 1.11**). The metal complexes developed from this ligand are expected to be in *C,N*-chelating mode. The steric effect of the 9-anthryl group towards the structures of the complexes synthesized will be studied.



42 **43**

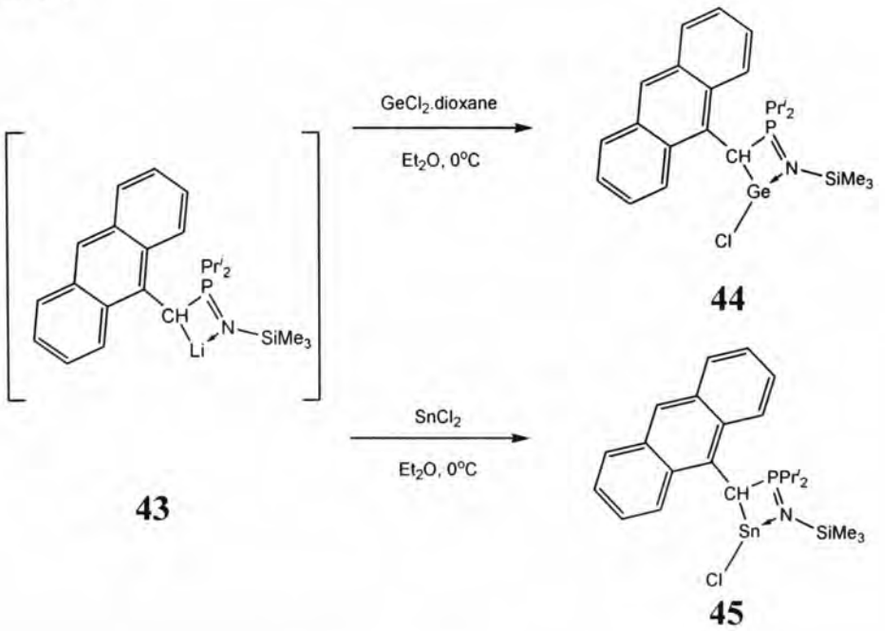
Figure 1.11

The monolithiated (9-anthryl)(iminophosphorano)methane (**43**) was prepared *in-situ* by metalation of neutral (9-anthryl)(iminophosphorano)methane with one equivalent of LiBu^n in diethyl ether.[5] In chapters 1 and 2, the intermediate lithium compound will act as a ligand transfer reagent to prepare several group 4 and 14 metal complexes. Their structures will be characterized by X-ray crystallography.

1.3 Results and Discussion

1.3.1.1 Synthesis of (9-Anthryl)(iminophosphorano)methanide Germanium(II) Chloride [Ge{CH(Pr^i_2P=NSiMe$_3$)(Anth)}Cl] (44) and (9-Anthryl)(iminophosphorano)methanide Tin(II) Chloride [Sn{CH(Pr^i_2P=NSiMe$_3$)(Anth)}Cl] (45)

The lithium complex **43** undergoes metathesis reaction with one equivalent of $GeCl_2$·dioxane and $SnCl_2$ in diethyl ether at 0°C to give group 14 metal complexes [Ge{CH(Pr^i_2P=NSiMe$_3$)(Anth)}Cl] (**44**) and [Sn{CH(Pr^i_2P=NSiMe$_3$)(Anth)}Cl] (**45**), respectively (**Scheme 1.3**). The yields of **44** and **45** were 7.89% and 12.2%, respectively. Since compound **43** was only prepared *in-situ* by lithiation of compound **42**, the percentage yield was not 100 %. Thus, it resulted in the low yields of compounds **44** and **45**.



43 **44** **45**

Scheme 1.3

1.3.1.2 Spectroscopic Properties of Complexes 44 and 45

Compounds **44** and **45** are both air and moisture sensitive yellow crystalline solids. Compound **44** is soluble in THF, Et_2O and toluene but only slightly soluble in hydrocarbon solvent. Meanwhile, compound **45** is soluble in CH_2Cl_2, THF and Et_2O but only slightly soluble in hydrocarbon solvent. They were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, elemental analysis and X-ray crystallography. Compound **45** was also characterized by ^{119}Sn NMR spectroscopy.

The ^1H NMR and ^{13}C NMR spectra of **44** and **45** displayed one set of signals corresponding to (9-anthryl)(iminophosphorano)methanide ligand, which is consistent with the solid-state structure. The ^{31}P NMR spectra of **44** and **45** showed one singlet signal at δ 31.45 and δ 31.54 ppm, respectively, which are also consistent with the solid state structure where one phosphorus environment is present. The ^{119}Sn NMR spectrum of **45** displayed one signal at δ 124.18 ppm, which is more downfield than that of $[HC(PPh_2{=}NSiMe_3)_2SnCl]$ (δ -139.21 ppm).[38] This may be due to the steric effect of the supporting ligand which stabilizes the complex.

1.3.1.3 Molecular Structures of [Ge{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}Cl] (44) and [Sn{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}Cl] (45)

The molecular structures of compounds **44** and **45** are shown in Figure 1.12 and

Figure 1.13, respectively. Selected bond distances (Å) and angles (deg) are listed in Table 1.1 and Table 1.2, respectively.

Compounds **44** and **45** are both isostructural and monomeric in the solid state. The metal centers in **44** and **45** are bonded to one (9-anthryl)(iminophosphorano)methanide ligand and both exhibit a trigonal pyramidal geometry. The ligand is coordinated to the metal centers in *C,N*-chelation forming a four-membered metallacycle. In compounds **44** and **45**, the germanium(II) and tin(II) centers are also bonded to one chlorine atom.

In compound **44**, the Ge-N_{amide} bond distance of 2.019 Å is slightly longer than that of 1.920(2) Å in [Ge{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl][39] as well as 1.993 Å (average) in [HC(PPh$_2$=NSiMe$_3$)$_2$GeCl][40]. The Ge-Cl bond distance of 2.331 Å is also comparable to that of 2.334(2) Å in [HC(PPh$_2$=NSiMe$_3$)$_2$GeCl][40], 2.283(9) Å in [Ge{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl][39] and 2.295(1) Å in [{HC(CMeNAr)$_2$}GeCl][41]. In compound **45**, the Sn-N_{amide} bond distance of 2.221 Å is slightly longer than that of 2.184 Å (average) in [{SnCl(Me$_3$SiNPPr$^i_2$CH)}$_2$C$_4$H$_2$N$_2$-2,3][20], 2.225(6) Å in [Sn{CH(Pr$^i_2$P=NSiMe$_3$)(2-Py)}Cl][42] as well as 2.256(6) Å in [{2-{Sn{C(Pr$^i_2$P=NSiMe$_3$)}}-6-{Sn{CH(Pr$^i_2$P=NSiMe$_3$)}Cl}}C$_5$H$_3$N]$_2$.[10] The Sn-Cl bond distance of 2.480 Å is also comparable to that of 2.466(2) Å in [SnCl{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}],[43] 2.472 Å in [{SnCl(Me$_3$SiNPPr$^i_2$CH)}$_2$C$_4$H$_2$N$_2$

-2,3][20] and 2.501(7) Å in [Sn{CH(Pr^i_2P=NSiMe$_3$)(2-Py)}Cl].[42]

The P(1)-C(1) bond distances of compounds **44** and **45** are 1.797 Å and 1.800 Å, respectively. They are both slightly shorter than that of 1.836 Å in the neutral ligand [CH_2(Pr^i_2P=NSiMe$_3$)(Anth)].[5] In addition, the P-N bond distances of compounds **44** and **45** are 1.607 Å and 1.613 Å, respectively, which are slightly longer than that of 1.528(2) Å in the neutral ligand.[5] These suggest that there is charge delocalization within the C-P-N skeleton of the ligand.

The average C-C bond distances within the anthryl group of compounds **44** and **45** are 1.399 Å and 1.402 Å, respectively. They are both slightly longer than that of 1.378 Å in the neutral ligand,[5] which indicates that charges within the C-P-N skeleton are more or less delocalized along the 9-anthryl group of the ligand.

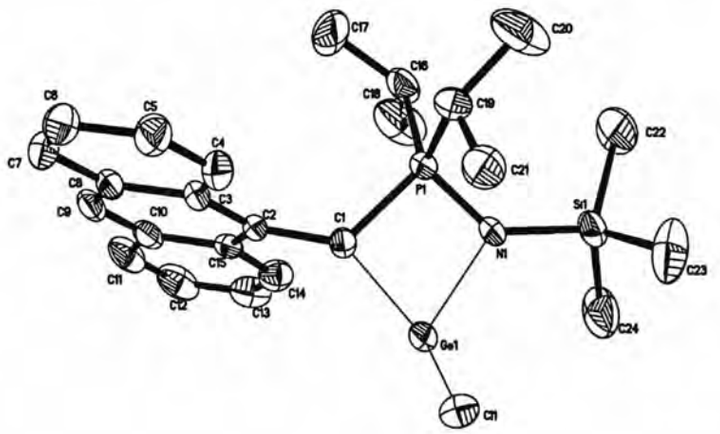


Figure 1.12 Molecular structure of [Ge{CH(Pr^i_2P=NSiMe$_3$)(Anth)}Cl] (**44**).

Table 1.1 Selected bond distances (Å) and angles (deg) for compound **44**

Ge(1)–N(1)	2.019(4)	Ge(1)-C(1)	2.134(5)
Ge(1)-Cl(1)	2.331(2)	Ge(1)-P(1)	2.740(2)
P(1)-N(1)	1.607(5)	P(1)-C(1)	1.797(5)
C(1)-C(2)	1.502(7)	C(2)-C(3)	1.402(8)
C(2)-C(15)	1.417(8)	C(3)-C(4)	1.440(8)
C(3)-C(8)	1.446(7)	C(4)-C(5)	1.347(8)
C(5)-C(6)	1.405(9)	C(6)-C(7)	1.331(9)
C(7)-C(8)	1.432(9)	C(8)-C(9)	1.379(9)
C(9)-C(10)	1.370(8)	C(10)-C(15)	1.438(8)
C(10)-C(11)	1.452(9)	C(11)-C(12)	1.361(1)
C(12)-C(13)	1.389(1)	C(13)-C(14)	1.352(9)
C(14)-C(15)	1.415(8)		
N(1)-Ge(1)-C(1)	76.3(2)	N(1)-Ge(1)-Cl(1)	100.1(1)
C(1)-Ge(1)-Cl(1)	95.5(2)	N(1)-Ge(1)-P(1)	35.6(1)
C(1)-Ge(1)-P(1)	41.0(1)	Cl(1)-Ge(1)-P(1)	103.1(6)
N(1)-P(1)-Ge(1)	46.9(2)	P(1)-N(1)-Ge(1)	97.5(2)
P(1)-C(1)-Ge(1)	87.9(2)	C(2)-C(1)-Ge(1)	128.6(4)

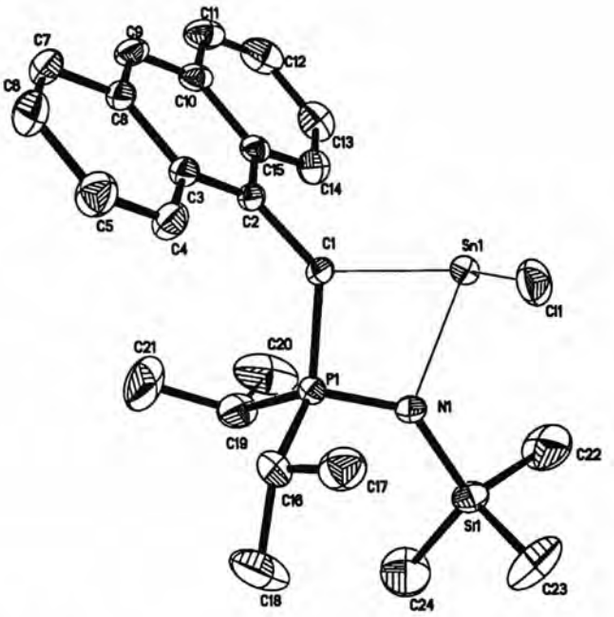


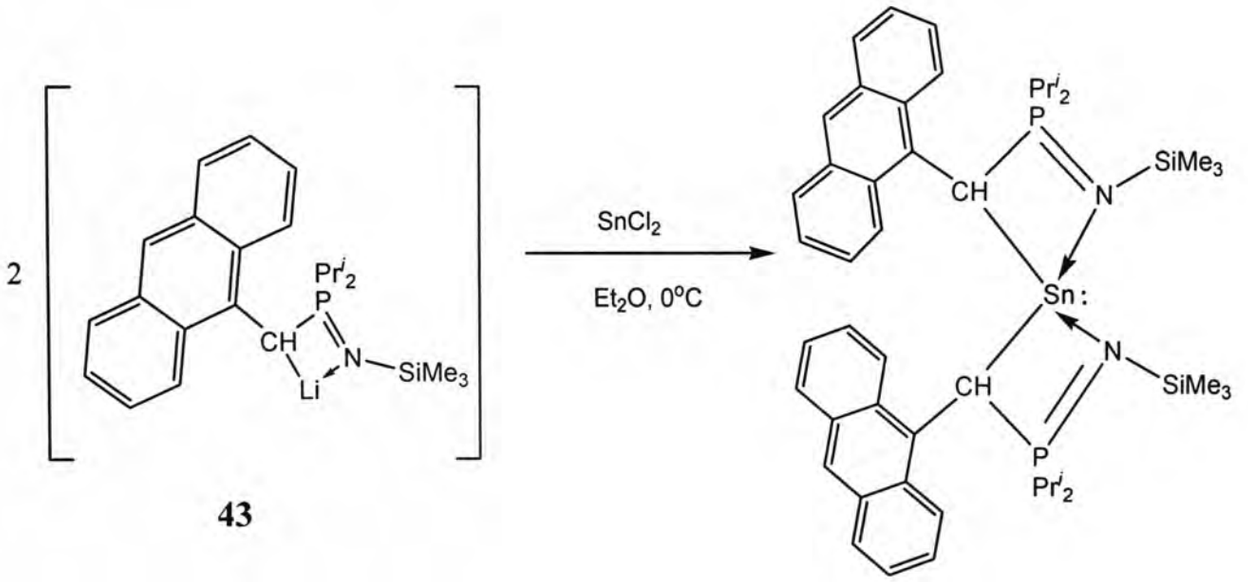
Figure 1.13 Molecular structure of [Sn{CH(Pr^i_2P=NSiMe$_3$)(Anth)}Cl] (**45**).

Table 1.2 Selected bond distances (Å) and angles (deg) for compound **45**

Sn(1)–N(1)	2.221(2)	Sn(1)-C(1)	2.306(3)
Sn(1)-Cl(1)	2.480(1)	Sn(1)-P(1)	2.930(9)
P(1)-N(1)	1.613(3)	P(1)-C(1)	1.800(3)
C(1)-C(2)	1.513(3)	C(2)-C(15)	1.413(4)
C(2)-C(3)	1.416(4)	C(3)-C(4)	1.435(4)
C(3)-C(8)	1.449(4)	C(4)-C(5)	1.354(5)
C(5)-C(6)	1.420(5)	C(6)-C(7)	1.343(5)
C(7)-C(8)	1.433(5)	C(8)-C(9)	1.378(4)
C(9)-C(10)	1.374(5)	C(10)-C(11)	1.435(5)
C(10)-C(15)	1.447(4)	C(11)-C(12)	1.349(6)
C(12)-C(13)	1.412(5)	C(13)-C(14)	1.361(4)
C(14)-C(15)	1.420(4)		
N(1)-Sn(1)-C(1)	70.8(9)	N(1)-Sn(1)-Cl(1)	99.7(7)
C(1)-Sn(1)-Cl(1)	93.1(8)	N(1)-Sn(1)-P(1)	33.1(6)
C(1)-Sn(1)-P(1)	37.9(7)	Cl(1)-Sn(1)-P(1)	99.8(3)
N(1)-P(1)-Sn(1)	48.6(9)	P(1)-N(1)-Sn(1)	98.5(1)
P(1)-C(1)-Sn(1)	90.2(1)	C(2)-C(1)-Sn(1)	126.9(2)

1.3.2.1 Synthesis of Homoleptic Dialkylstannylene [Sn{CH(Pr^i_2P=NSiMe$_3$)(Anth)}$_2$] (46)

The lithium complex **43** undergoes metathesis reaction with $SnCl_2$ in a 2 : 1 ratio in diethyl ether at 0°C to give a homoleptic dialkylstannylene, [Sn{CH(Pr^i_2P=NSiMe$_3$)(Anth)}$_2$] (**46**) (**Scheme 1.4**). Compound **46** is an orange crystalline solid with a yield of 5.15%.



43 **46**

Scheme 1.4

1.3.2.2 Spectroscopic Properties of 46

Compound **46** is an extremely air and moisture sensitive orange crystalline solid. It is soluble in THF, Et_2O and toluene but only sparingly soluble in hexane. It was characterized by ^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR spectroscopy, elemental analysis and X-ray crystallography..

The ^{1}H NMR and ^{13}C NMR spectra of **46** displayed one set of signals due to the supporting ligand, which is consistent with the solid-state structure. It is also suggested that the two anthryl ligands of the complex are homoleptic and have the same chemical environment. The ^{31}P NMR spectrum showed one singlet signal at δ 50.92 ppm, which also supports that the ligands are in the same chemical environment. The ^{119}Sn NMR spectrum displayed a peak at δ 11.18 ppm.

1.3.2.3 Molecular Structure of [Sn{CH(Pr^{i}_2P=NSiMe$_3$)(Anth)}$_2$] (46)

The molecular structure of compound **46** is shown in Figure 1.14. Selected bond distances (Å) and angles (deg) are listed in Table 1.3.

Compound **46** is a monomeric carbene analogue. The metal center in **46** is bonded to two (9-anthryl)(iminophosphorano)methanide ligands and they are coordinated to the metal center in a *trans C,N*-chelation. It shows a seesaw geometry which is in good agreement with stereochemically active lone pair at the metal. The

average bite angle C-Sn-N of 66.9° is larger than the C-Sn-N angle of 58.0(6)° in $[Sn\{N(SiMe_3)C(Bu^t)C(H)SiMe_3\}_2]$.[44] The sum of angles subtended at the metal center is 317.1°, which is comparable to that of 317.2° in $[Sn\{CH(SiMe_3)(C_9H_6N\text{-}8)\}_2]$.[45] The $Sn\text{-}N_{amide}$ bond distances of 2.538 Å and 2.570 Å in **46** are comparable to that of 2.510(2) Å in $[Sn\{N(SiMe_3)C(Bu^t)C(H)SiMe_3\}_2]$[44] but are significantly shorter than the average distance of 2.168 Å in $[Sn\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2]$.[39]

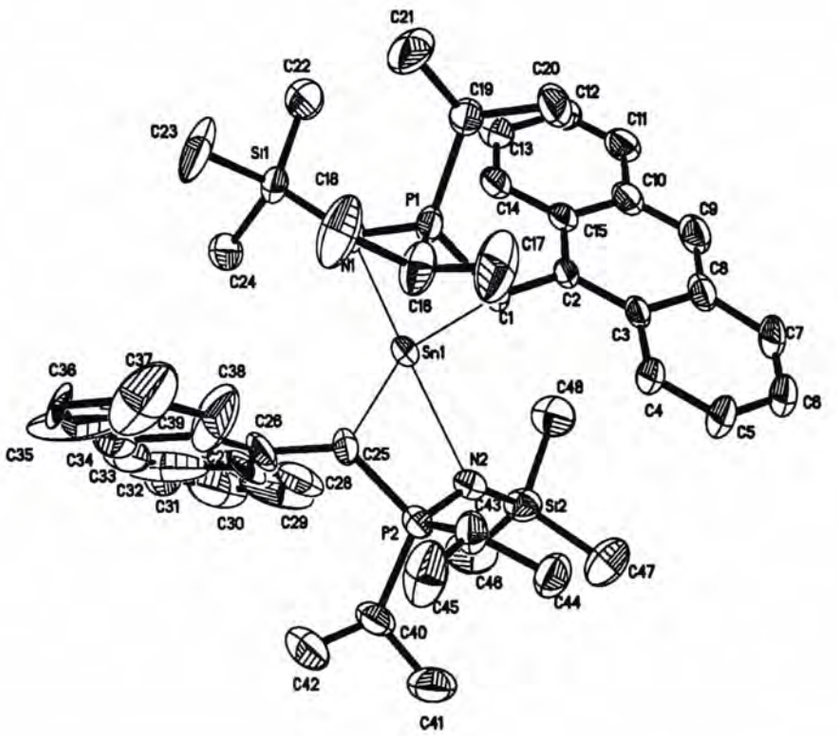


Figure 1.14 Molecular structure of $[Sn\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2]$ (**46**).

Table 1.3 Selected bond distances (Å) and angles (deg) for compound **46**

Sn(1)–C(1)	2.340(8)	Sn(1)-C(25)	2.342(9)
Sn(1)-N(1)	2.538(7)	Sn(1)-N(2)	2.570(7)
C(1)-Sn(1)-C(25)	101.6(3)	C(1)-Sn(1)-N(1)	67.2(2)
C(25)-Sn(1)-N(1)	91.0(3)	C(1)-Sn(1)-N(2)	92.3(3)
C(25)-Sn(1)-N(2)	66.6(3)	N(1)-Sn(1)-N(2)	146.6(2)
P(1)-N(1)-Sn(1)	92.6(3)	P(2)-N(2)-Sn(1)	92.1(3)
P(1)-C(1)-Sn(1)	93.7(3)	P(2)-C(25)-Sn(1)	94.7(4)

1.4 Experimental Section

Materials: 9-anthracarboxaldehyde, lithium wire, chlorodiisopropylphosphine, Me_3SiN_3, $LiBu^n$, $GeCl_2$·dioxane, $SnCl_2$ were purchased from Aldrich Chemical Co. and used without further purification.

Preparation of [Ge{CH(Pr^i_2P=NSiMe_3)(Anth)}Cl] (Anth = 9-anthryl) (44)

A solution of [Li{CH(Pr^i_2P=NSiMe_3)(Anth)}] (**43**) prepared from the lithiation of [CH_2(Pr^i_2P=NSiMe_3)(Anth)] (**42**) (0.27g, 0.68mmol) in Et_2O (30mL) was added slowly to the solution of $GeCl_2$·dioxane (0.20g, 0.87mmol) in Et_2O (30mL) at 0°C. The yellow solution was raised to ambient temperature and stirred for 12 hrs. The volatiles were removed under reduced pressure and the residue was extracted with toluene. The yellow solution mixture was filtered and concentrated upon cooling of the filtrate at 0°C, yellow crystals of the title compounds were obtained. Yield: 0.03g (7.89%). Mp: 294.1 – 298.5°C. Anal. Calcd (%) for $C_{24}H_{33}ClGeNPSi$: C, 57.35; H, 6.62; N, 2.79; Found: C, 54.50; H, 6.74; N, 3.12. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.40 (s, 9H, Si*Me*$_3$), 1.19 (dd, J = 7.2, 9.6 Hz, 6H, CH*Me*$_2$), 1.40 (dd, J = 7.2, 9.0 Hz, 6H, CH*Me*$_2$), 2.34-2.48 (m, 2H, C*H*Me$_2$), 3.83 (d, J = 12.9 Hz, C*H*), 7.30 (t, J = 6.6 Hz, 2H, Anth), 7.40 (t, J = 8.7 Hz, 2H, Anth), 7.86 (d, J = 3.9 Hz, 2H, Anth), 8.10 (s, 1H, Anth), 8.62 (d, J = 9.0 Hz, 2H, Anth). ^{13}C {^{1}H} NMR (C_6D_6): δ (ppm) 5.10 (Si*Me*$_3$), 15.69 (CH*Me*$_2$), 28.04 (*C*H), 28.86 (*C*HMe$_2$), 125.56, 125.90, 126.96, 128.06, 128.38, 128.70, 129.69, 130.27 (Anth). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 31.45.

Preparation of [Sn{CH(Pr^i_2P=NSiMe_3)(Anth)}Cl] (Anth = 9-anthryl) (45)

A solution of [Li{CH(Pr^i_2P=NSiMe_3)(Anth)}] (**43**) prepared from the lithiation of [CH_2(Pr^i_2P=NSiMe_3)(Anth)] (**42**) (0.36g, 0.90mmol) in Et_2O (30mL) was added

slowly to the solution of $SnCl_2$ (0.17g, 0.90mmol) in Et_2O (30mL) at 0°C. The yellow solution was raised to ambient temperature and stirred for 12 hrs. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2. The filtrate was added with THF (*c.a.* 2mL) and concentrated to afford **45** as yellow crystals. Yield: 0.01g (12.2%). Mp: 168.0 – 172.0°C. Anal. Calcd (%) for $C_{24}H_{33}ClNPSiSn$: C, 52.53; H, 6.06; N, 2.55; Found: C, 50.54; H, 6.12; N, 2.96. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.25 (s, 9H, Si*Me*$_3$), 1.08 (dd, J = 6.0, 9.0 Hz, 6H, CH*Me*$_2$), 1.35 (dd, J = 6.0, 9.0 Hz, 6H, CH*Me*$_2$), 2.23-2.35 (m, 2H, C*H*Me$_2$), 3.73 (d, J = 15.0 Hz, C*H*), 7.25 (t, J = 3.0 Hz, 2H, Anth), 7.28 (t, J = 6.0 Hz, 2H, Anth), 7.80 (d, J = 3.0 Hz, 2H, Anth), 8.52 (s, 1H, Anth), 8.66 (d, J = 6.0 Hz, 2H, Anth). ^{13}C {^{1}H} NMR (C_6D_6): δ (ppm) 5.12 (Si*Me*$_3$), 16.04 (CH*Me*$_2$), 28.04 (*C*H), 30.93 (*C*HMe$_2$), 125.07, 125.98, 126.98, 131.61, 132.85, 132.90, 134.46, 134.55 (Anth). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 31.54. ^{119}Sn {^{1}H} NMR (C_6D_6): δ (ppm) 124.18.

Preparation of [Sn{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}$_2$] (Anth = 9-anthryl) (46)

A solution of [Li{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}] (**43**) prepared from the lithiation of [CH_2(Pr$^i_2$P=NSiMe$_3$)(Anth)] (**42**) (0.48g, 1.21mmol) in Et_2O (30mL) was added slowly to the solution of $SnCl_2$ (0.22g, 1.17mmol) in Et_2O (30mL) at 0°C. The yellow solution was raised to ambient temperature and stirred for 12 hrs. The mixture was filtered and the filtrate was added with hexane (*c.a.* 5mL). The resulting light orange solution was concentrated to give **46** as orange crystals. Yield: 0.05g (5.15%). Mp: 140.0°C (dec.). Anal. Calcd (%) for $C_{48}H_{66}N_2P_2Si_2Sn$: C, 63.50; H, 7.33; N, 3.09; Found: C, 62.69; H, 7.69; N, 3.44. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) -0.41 (s, 18H, Si*Me*$_3$), 0.69 (dd, J = 6.0, 9.0 Hz, 12H, CH*Me*$_2$), 1.37 (dd, J = 6.0, 9.0 Hz, 12H, CH*Me*$_2$), 2.32-2.35 (m, 4H, C*H*Me$_2$), 3.73 (d, J = 12.0 Hz, C*H*), 7.27 (t, J = 3.0 Hz,

4H, Anth), 7.45 (t, J = 6.0 Hz, 4H, Anth), 7.84 (d, J = 6.0 Hz, 4H, Anth), 8.68 (s, 2H, Anth), 9.50 (d, J = 9.0 Hz, 4H, Anth). ^{13}C $\{^1H\}$ NMR (C_6D_6): δ (ppm) 4.61 (Si*Me*$_3$), 17.09 (CH*Me*$_2$), 32.80 (*C*H), 36.14 (*C*HMe$_2$), 123.64, 124.37, 125.06, 125.18, 131.78, 133.27, 133.54, 138.60 (Anth). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 50.92. ^{119}Sn $\{^1H\}$ NMR (C_6D_6): δ (ppm) 11.18.

1.5 References for Chapter 1

1. Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1999**, *2*, 635

2. Johnson, A. W. *Ylides and Imines of Phosphorus*, Wiley, New York, **1993**

3. Steiner, A.; Zacchini, S.; Richards, P. I. *Coord. Chem Rev.* **2002**, *227,* 193

4. Fei, Z.; Dyson, P. J. *Coord. Chem. Rev.* **2005**, *249*, 2056

5. Wong, K.-W. *Ph. D. Thesis, The Chinese University of Hong Kong,* **2006**

6. Ong, C. M.; McKarns, P.; Stephan, D. W. *Organometallics* **1999**, *18*, 4197

7. Wang, Z.-X.; Qi, C.Y. *Dalton. Trans.* **2005**, 996

8. Kamalesh Babu, R. P.; Aparna, K.; McDonald, R.; Cavell, R. G. *Organometallics* **2001**, *20*, 1451

9. Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Mak, T. C. W. *Angew. Chem. Int. Ed.* **2001**, *40*, 2501

10. Leung, W.-P.; Ip, Q. W.-Y.; Wong, S.–Y.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4604

11. Boubukeur, L.; Ulmer, S.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2006**, *25*, 315

12. Buchard, A.; Komly, B.; Auffrant, A.; Le Goff, X. F.; Le Floch, P. *Organometallics*, **2008**, *27*, 4380

13. Katti, K. V. ; Santarsiero, B. D.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.*

1993, *32*, 5919

14. Wang, Z.-X.; Li, Y.-X. *Organometallics* **2003**, *22*, 4900

15. Ghesner, I.; Fenwick, A.; Stephan, D. W. *Organometallics* **2006**, *25*, 4985

16. Qi, C.; Zhang, S. *J. Organomet. Chem.* **2006**, *691*, 1154

17. Maurer, A.; Fenske, D.; Beck, J.; Hiller, W.; Strahle, J.; Bohm, E.; Dehnicke, K. *Z. Naturforsch. B* **1988**, *43*, 1

18. Wong, S.-Y. *M. Phil. Thesis, The Chinese University of Hong Kong*, **2002**

19. Sze, W.-Y. *M. Phil. Thesis, The Chinese University of Hong Kong*, **2005**

20. Leung, W.-P.; Chan, K.-P.; Kan, K.-W.; Mak, T. C. W. *Organometallics* **2008**, *27*, 2767

21. Wei, P.; Stephan, D. W. *Organometallics* **2003**, *22*, 601

22. Orzechowski, L.; Jansen, G.; Harder, S. *J. Am. Chem. Soc.* **2006**, *128*, 14676

23. Orzechowski, L.; Harder, S. *Organometallics,* **2007**, *26*, 5501

24. Chai, Z.-Y.; Zhang, C.; Wang, Z.-X. *Organometallics* **2008**, *27*, 1626

25. Evans, D. J.; Hill, M. S.; Hitchcock, P. B. *Dalton Trans.*, **2003**, 570

26. Gamer, M. T.; Dehnen, S.; Roesky, P. W. *Organometallics* **2001**, *20*, 4230

27. Kasani, A.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1483

28. Jones, N. D.; Cavell, R. G. *J. Organomet. Chem.* **2005**, *690*, 5485

29. Cavell, R. G.; Kamalesh Babu, R. P.; Kasani, A.; McDonald, R. *J. Am. Chem. Soc.* **1999**, *121*, 5805

30. Kasani, A.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **1999**, 1993

31. Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc. Dalton, Trans.* **1976**, 2268

32. Harrison, P. G. *Coord. Chem. Rev.* **1976**, *20*, 1

33. Connolly, J. W.; Hoff, C. *Adv. Organomet. Chem.* **1981**, *19*, 123

34. Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311

35. Driess, M.; Grutzmacher, H. *Angew. Chem. Int. Ed.* **1996**, *35*, 828

36. Wingerter, S.; Gornitzka, H.; Bertermann, R.; Pandey, S. K.; Rocha, J.; Stalke, D. *Organometallics* **2000**, *19*, 3890

37. Wang, Z.-X.; Li, Y.-X. *Organometallics* **2002**, *21*, 4641

38. Kan, K.-W. *Ph. D. Thesis, The Chinese University of Hong Kong,* **2007**

39. Leung, W.-P.; So, C.-W.; Wu, Y.-S.; Li, H.-W.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2005**, 513

40. Leung, W.-P.; So, C.-W.; Wang, Z.-X.; Wang, J.-Z.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4305

41. Ding, Y.; Roesky, H. W.; Noltemeyer, M; Schmidt, H.-G.; Power, P. P. *Organometallics* **2001**, *20*, 1190

42. Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Yang, Q.-C.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001**, *123*, 8123

43. Al-Juaid, S. S.; Avent, A. G.; Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Patel, D. J.; Smith, J. D. *Organometallics* **2001**, *20*, 1223

44. Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Layh, M.; Severn, J. *J. Chem. Soc. Chem. Commun.* **1997**, 1189

45. Leung, W.-P; Kwok, W.-H.; Weng, L.-H.; Law. L. T. C.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, *22*, 4301

CHAPTER 2

SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDY OF (9-ANTHRYL)(IMINOPHOSPHORANO)METHANIDE GROUP 4 METAL COMPLEXES

2.1 Introduction

2.1.1 A General Review of Group 4 Metallocene Catalysts in Olefin Polymerization

Group 4 metallocenes Cp_2MX_2 have been used as homogenous Ziegler-Natta catalysts in olefin polymerization. They are capable of polymerizing olefins and dienes under suitable temperature and pressure.[1] The development of these compounds has led to a new generation of polymerization catalysts. For example, a series of metallocene catalysts, Cp_2MCl_2 (M = Ti, Zr and Hf) have been developed recently, which are highly efficient at polymerizing α-olefin (e.g. ethylene and propene) in the presence of alumoxanes.[2] Organometallic complexes formed by zirconocene/methylalumoxane(MAO) are notably the most active Ziegler-Natta catalysts known today.[1, 3, 4] In the Cp_2ZrCl_2/MAO system, the role of MAO as cocatalyst still remains unknown, but it has been suggested (1) to alkylate the catalyst,[2, 5, 6] (2) to prevent the biomolecular reduction of the catalyst[2, 3, 6, 7] and (3) to act as a counter-ion to stabilize the cationic metallocene alkyl.[2, 5] It is also believed

that the intermediate, $[Cp_2ZrMe]^+$, formed during the reaction of Cp_2ZrCl_2 with MAO, provides an active site for polymerization.[2] Its derivatives, $[Cp_2ZrH]^+$ and $[Cp_2Zr(CH_2CH_2R)]^+$ are also active species in the process.[8, 9]

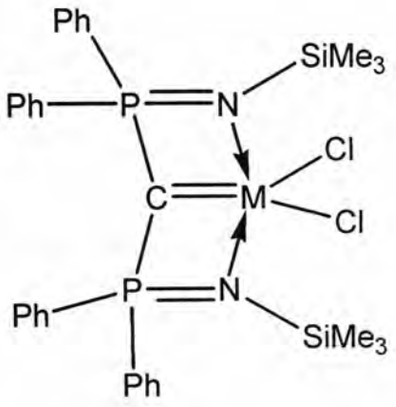
2.1.2 A General Review of Group 4 Metal Complexes

Breslow and coworkers reported the catalytic activity of bis(cyclopentadienyl)-titanium dichloride for the polymerization of ethylene in 1957.[10,11] Since then, the exploration of polymerization catalysts using group 4 metallocenes has drawn much attention. However, there is much difficulty in establishing the fundamental trends of metallocene catalytic activity due to the steric and electronic effect of ligand substituents.[12] This leads to the development of group 4 transition metal complexes as 'non-metallocene' catalysts for olefin polymerization.[13,14] In recent years, a number of group 4 early transition metal complexes having heteroatoms ligands which are potential polymerization catalysts have been reported.[15-19]

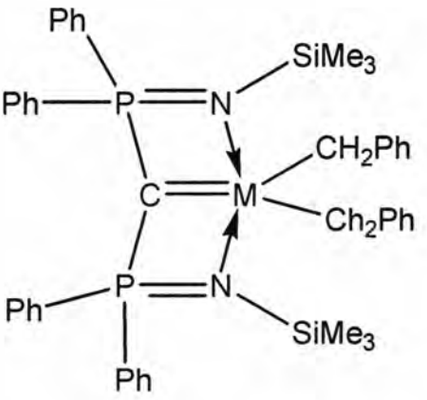
In particular, phosphoranoimine and/or phosphinimide ligands are often incorporated to synthesize group 4 metal complexes for use as a new family of highly active olefin polymerization catalysts. Stephan and coworkers have developed a number of group 4 metal complexes which are highly active in olefin polymerization

over the past decade.[20-28]

Apart from that, Cavell and coworkers have successfully synthesized a series of 'pincer' type group 4 bis(phosphinimine) complexes which possess the M=C carbene-ylide structure. For example, $[MCl_2\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}]$ [M = Ti (**47**), Zr (**48**), Hf (**49**)][29, 30] and $[M\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}(CH_2Ph)_2]$ [M = Zr (**50**), Hf (**51**)][31, 32] have been reported (**Figure 2.1**). In 2001, they reported the first zirconium biscarbene complex, $[Zr\{C(Me_2P{=}NSiMe_3)_2\}_2]$ (**52**) (**Figure 2.2**). The biscarbene complex can be formed, if and only if, the phosphorus center contains methyl groups but not other bulky substituents, e.g. Ph or Cy groups.[33]



M = Ti (**47**), Zr (**48**), Hf (**49**)



M = Zr (**50**), Hf (**51**)

Figure 2.1

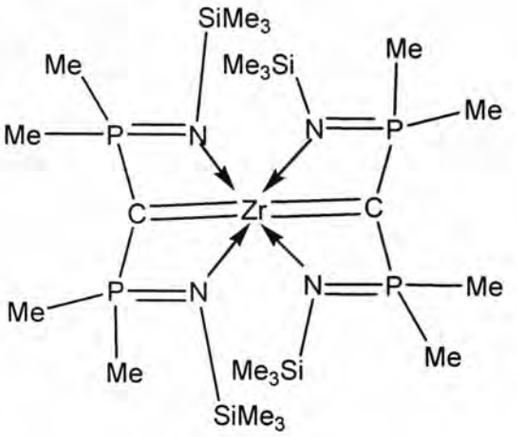


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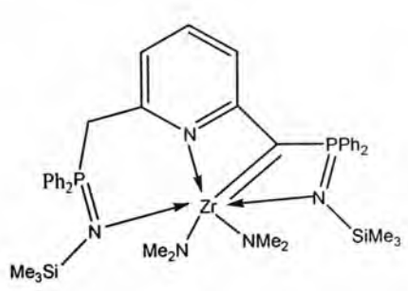
Figure 2.2

Our group has previously synthesized Zr and Hf metal complexes containing phosphoranoimine ligands. For example, $[Zr\{(Me_3SiNPPh_2C)(Me_3SiN{=}PPh_2CH_2)C_5H_3N\text{-}2,6\}(NMe_2)_2]$ (**53**)[34], $[(Me_2N)_2M\{CH(Ph_2PN)(2\text{-}Py)\}]_2$ [M = Zr (**54**), Hf (**55**)][35], and $[\{HfCl_3(Me_3SiNPPr^i{}_2CH)\}_2C_4H_2N_2\text{-}2,3]$ (**56**)[36] have been reported (**Figure 2.3**). The catalytic activities of compounds **54-56** towards ethylene polymerization have also been studied.[35, 36]



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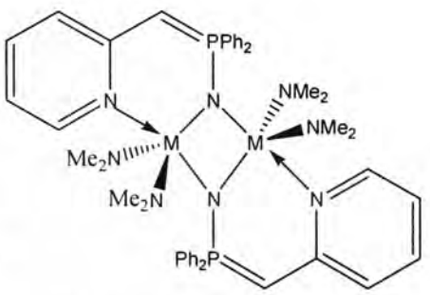

M = Zr (**54**), Hf (**55**)

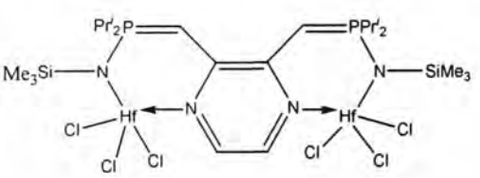

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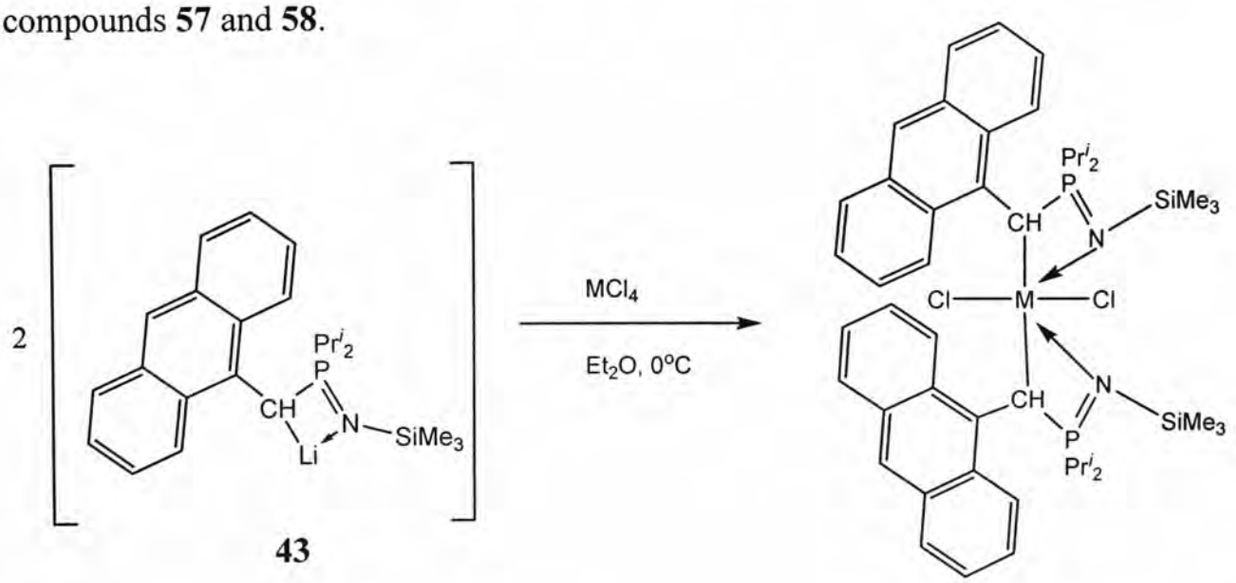
Figure 2.3

2.2 Results and Discussion

2.2.1.1 Synthesis of (9-Anthryl)(iminophosphorano)methanide Zirconium(IV) Dichloride $[Zr\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2Cl_2]$ (57) and (9-Anthryl)(iminophosphorano)methanide Hafnium(IV) Dichloride $[Hf\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2Cl_2]$ (58)

The lithium complex **43** undergoes metathesis reaction with $ZrCl_4$ and $HfCl_4$ in a 2 : 1 ratio in diethyl ether at 0°C to give group 4 metal complexes $[Zr\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2Cl_2]$ (**57**) and $[Hf\{CH(Pr^i_2P{=}NSiMe_3)(Anth)\}_2Cl_2]$ (**58**), respectively (**Scheme 2.1**). The yields of **57** and **58** were 14.68% and 15.16% respectively. Since compound **43** was only prepared *in-situ* by lithiation of compound **42**, the percentage yield was not 100 %. Thus, it resulted in the low yields of compounds **57** and **58**.



43

M = Zr (**57**), Hf (**58**)

Scheme 2.1

2.2.1.2 Spectroscopic Properties of 57 and 58

Compounds **57** and **58** are both air and moisture sensitive yellow crystalline solids. Compounds **57** and **58** are both soluble in THF and CH_2Cl_2 but only slightly soluble in hexane. They were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, elemental analysis and X-ray crystallography.

The ^1H NMR and ^{13}C NMR spectra of **57** and **58** displayed one set of signals due to the supporting ligand, which is consistent with the solid-state structure. It is also suggested that the two supporting ligands of the complex are homoleptic and have the same chemical environment. The ^1H NMR spectra of **57** and **58** displayed signals which can be assigned to the 9-anthryl, iminophosphorano and methyl groups of the ligand.

The ^{31}P NMR spectra of **57** and **58** showed one singlet signal at δ 67.57 ppm and δ 63.80 ppm, respectively. This supports that the two phosphorus atoms in both **57** and **58** are in the same chemical environment.

2.2.1.3 Molecular Structures of [Zr{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}$_2$Cl$_2$] (57) and [Hf{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}$_2$Cl$_2$] (58)

The molecular structures of compounds **57** and **58** are shown in Figure 2.4 and Figure 2.5, respectively. Selected bond distances (Å) and angles (deg) are listed in

Table 2.1 and Table 2.2, respectively.

Compounds **57** and **58** are monomeric dichlorozirconium(IV) and dichlorohafnium(IV) compounds respectively. The metal centers of both **57** and **58** are bonded to two chloride ligands and coordinated to two ligands in *C,N*-chelation fashion forming two four-membered metallacycles. Both of them have a distorted octahedral geometry about the metal centers.

In compound **57**, the average Zr-Cl distance of 2.448 Å is similar to those of 2.513 Å in $[Zr\{N(SiMe_3)C(Bu^t)C(H)(C_5H_4N\text{-}2)\}_2Cl_2]$[37], 2.442 Å in $[ZrCl_2\{CH(Ph_2P{=}NSiMe_3)(C_6H_5)\}_2]$[25] and 2.445 Å in $[Zr\{P(Ph)C(=CHPh)P(Me)_2{=}NSiMe_3\}_2Cl_2]$[38]. The average P-C(methine) distance of 1.771(8) Å is shorter than that of 1.836(2) Å in the neutral ligand, $[CH_2(Pr^i_2P{=}NSiMe_3)(Anth)]$[25], and the average P-N distance of 1.606 Å is longer than that of 1.528 Å in the ligand. It suggests that charge delocalization is likely present within the C-P-N skeleton.

In compound **58**, the average Hf-Cl distance of 2.438 Å is similar to those of 2.424 Å in $[Hf\{N(SiMe_3)C(Bu^t)C(H)(C_5H_4N\text{-}2)\}_2Cl_2]$[37] and 2.420 Å in $[Hf\{P(Ph)C(=CHPh)P(Me)_2{=}NSiMe_3\}_2Cl_2]$[38]. The average P-C(methine) distance of 1.784 Å is also shorter than that of 1.836(2) Å in the neutral ligand, $[CH_2(Pr^i_2P{=}NSiMe_3)(Anth)]$[25], and the average P-N distance of 1.612 Å is also longer than that of 1.528 Å in the ligand. It suggests that charge delocalization is present

within the C-P-N skeleton as observed in compound **57**.

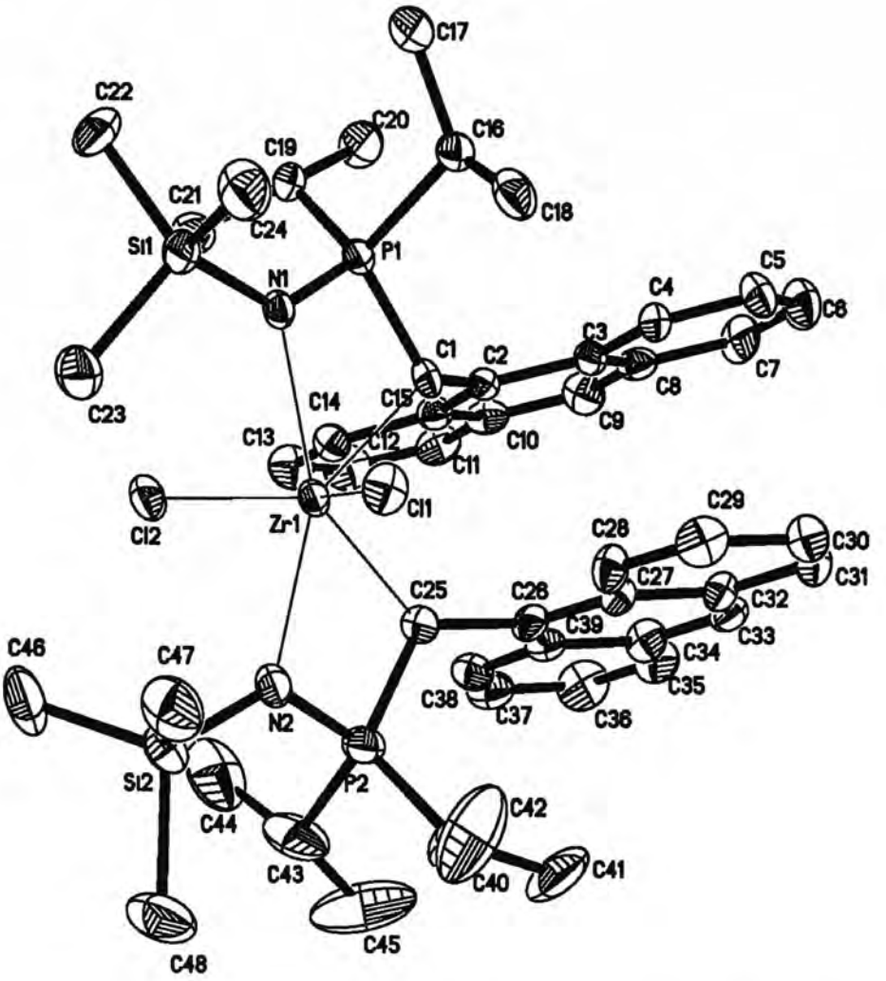


Figure 2.4 Molecular structure of [Zr{CH(Pr^i_2P=NSiMe$_3$)(Anth)}$_2$Cl$_2$] (**57**).

Table 2.1 Selected bond distances (Å) and angles (deg) for compound **57**

Zr(1)-N(1)	2.266(6)	Zr (1)-N(2)	2.270(7)
Zr(1)-C(1)	2.374(7)	Zr(1)-C(25)	2.378(8)
Zr(1)-Cl(2)	2.441(2)	Zr(1)-Cl(1)	2.455(2)
Zr(1)-P(2)	3.002(3)	Zr(1)-P(1)	3.016(2)
P(1)-N(1)	1.605(6)	P(2)-N(2)	1.606(7)
P(1)-C(1)	1.771(8)	P(2)-C(25)	1.770(8)
C(1)-C(2)	1.505(1)	C(25)-C(26)	1.512(1)
N(1)-Zr(1)-C(1)	67.2(2)	N(1)-Zr(1)-C(25)	144.9(2)
N(1)-Zr(1)-Cl(1)	81.6(2)	N(1)-Zr(1)-Cl(2)	86.3(2)
N(1)-Zr(1)-N(2)	147.3(2)	C(1)-Zr(1)-C(25)	77.7(3)
N(2)-Zr(1)-C(1)	145.5(2)	C(1)-Zr(1)-Cl(1)	104.5(2)
C(1)-Zr(1)-Cl(2)	104.6(2)	N(2)-Zr(1)-C(25)	67.8(3)
C(25)-Zr(1)-Cl(1)	108.9(2)	C(25)-Zr(1)-Cl(2)	102.3(2)
N(2)-Zr(1)-Cl(2)	85.6(2)	Cl(2)-Zr(1)-Cl(1)	140.9(9)
N(1)-P(1)-C(1)	98.9(3)	N(2)-P(2)-C(25)	100.4(4)

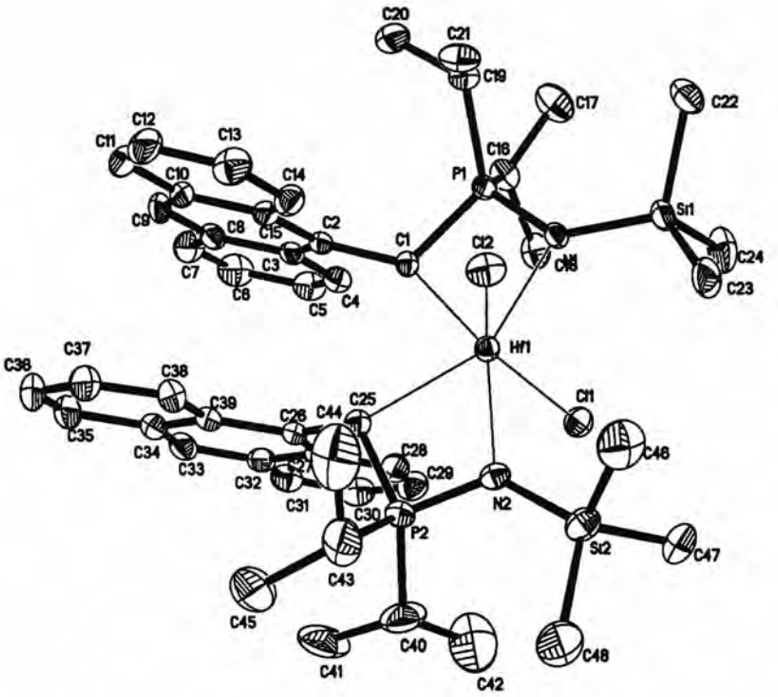


Figure 2.5 Molecular structure of [Hf{CH(Pr^i_2P=NSiMe$_3$)(Anth)}$_2$Cl$_2$] (**58**).

Table 2.2 Selected bond distances (Å) and angles (deg) for compound **58**

Hf(1)-N(1)	2.249(3)	Hf(1)-N(2)	2.262(3)
Hf(1)-C(1)	2.366(4)	Hf(1)-C(25)	2.378(4)
Hf(1)-Cl(2)	2.429(1)	Hf(1)-Cl(1)	2.447(1)
Hf(1)-P(2)	3.000(1)	Hf(1)-P(1)	3.012(1)
P(1)-N(1)	1.611(3)	P(2)-N(2)	1.612(4)
P(1)-C(1)	1.782(4)	P(2)-C(25)	1.785(4)
C(1)-C(2)	1.505(5)	C(25)-C(26)	1.503(6)
N(1)-Hf(1)-C(1)	67.6(1)	N(1)-Hf(1)-C(25)	145.9(1)
N(1)-Hf(1)-Cl(1)	81.6(9)	N(1)-Hf(1)-Cl(2)	86.2(9)
N(1)-Hf(1)-N(2)	145.7(1)	C(1)-Hf(1)-C(25)	78.3(1)
N(2)-Hf(1)-C(1)	84.5(9)	C(1)-Hf(1)-Cl(1)	104.6(1)
C(1)-Hf(1)-Cl(2)	104.5(1)	N(2)-Hf(1)-C(25)	68.3(1)
C(25)-Hf(1)-Cl(1)	108.6(1)	C(25)-Hf(1)-Cl(2)	102.1(1)
N(2)-Hf(1)-Cl(2)	85.3(9)	Cl(2)-Hf(1)-Cl(1)	141.2(4)
N(1)-P(1)-C(1)	98.4(2)	N(2)-P(2)-C(25)	100.2(2)

2.3 Catalytic Study of (9-Anthryl)(iminophosphorano)methanide Group 4 Metal Complexes on Ethylene Polymerization

The catalytic activities of compounds **57** and **58** towards ethylene polymerization were studied and the results are shown in Table 2.3 (The catalytic activity of Cp_2ZrCl_2 was also studied for comparison).

Table 2.3 Catalytic activities of compounds **57** and **58** on ethylene polymerization

compound (precatalyst)	amount of precatalyst used (μmol)	PE yield (g)	activity ($gmmol^{-1}h^{-1}$)
57	2.0	0.008	4.0
58	1.3	0	/
Cp_2ZrCl_2	32.8	3.90	118.9

The amount of compounds **57** and **58** was just sufficient for the catalytic study due to the low yields of the reactions. Compound **57** showed low activity towards ethylene polymerization when compared to that of the conventional zirconocene dichloride complex [Cp_2ZrCl_2].[29] Compound **58** showed no activity in ethylene polymerization upon stirring for 1 hour. The little amount of precatalysts used may be accounted for the low activities, though both compounds have a highly conjugated

system in the M-C-P-N [M = Zr (**57**), Hf (**58**)] ring. The reason for these results obtained might be due to the steric effect of the anthryl group of the ligands at the metal center, which hinders the formation of the cationic species with MAO. Similar suggestion of the steric effect of the ligands towards the formation of zwitterionic cationic species has been described before.[39]

The catalytic activity of zirconium(IV) complex **57** is higher than its analogous hafnium(IV) complex **58**. This is consistent with the reported catalytic studies of group 4 metal complexes.[29, 37]

The experimental setup shown in Figure 2.6 was modified from that described by our group before.[27] ^{n}BuLi has been used as the drying agent for ethylene gas instead of Drierite.

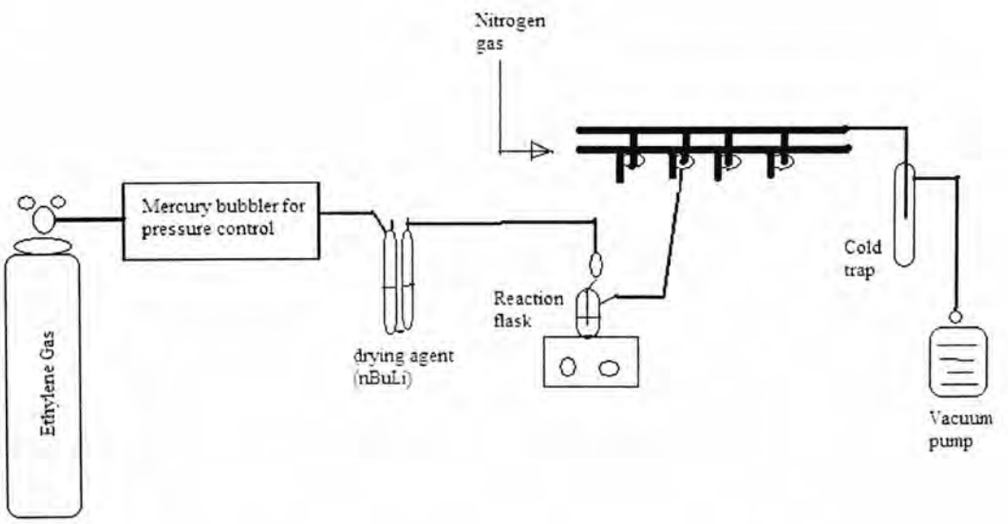


Figure 2.6 Experimental setup: ethylene polymerization

2.4 Experimental Section

Materials: LiBu^n, 9-anthracarboxaldehyde, lithium wire, chlorodiisopropylphosphine, Me_3SiN_3, $ZrCl_4$ and $HfCl_4$ were purchased from Aldrich Chemical Co. and used without further purification.

Preparation of [Zr{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}$_2$Cl$_2$] (Anth = 9-anthryl) (57)

A solution of [Li{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}] (**43**) prepared from the lithiation of [CH_2(Pr$^i_2$P=NSiMe$_3$)(Anth)] (**42**) (0.40g, 1.03mmol) in Et_2O (30 mL) was added slowly to the solution of $ZrCl_4$ (0.15g, 0.50mmol) in Et_2O (30 mL) at 0°C. The yellow solution was raised to ambient temperature and stirred for 12 hrs. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2. The filtrate was added with THF (*c.a.* 2mL) and concentrated to afford **57** as yellow crystals. Yield: 0.08g (14.68%). Mp: 294.1 – 298.5°C. Anal. Calcd (%) for $C_{48}H_{66}Cl_2N_2P_2Si_2Zr$: C, 60.60; H, 6.99; N, 2.94; Found: C, 59.04; H, 7.04; N, 3.55. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.71 (s, 18H, Si*Me*$_3$), 0.85 (dd, J = 6.0, 9.0 Hz, 12H, CH*Me*$_2$), 1.23 (dd, J = 6.0, 9.0 Hz, 12H, CH*Me*$_2$), 1.88-1.92 (m, 4H, C*H*Me$_2$), 3.05 (d, J = 15.0 Hz, C*H*), 6.50 (t, J = 9.0 Hz, 4H, Anth), 6.75 (t, J = 9.0 Hz, 4H, Anth), 7.36 (d, J = 9.0 Hz, 4H, Anth), 7.81 (s, 2H, Anth), 8.52 (d, J = 9.0 Hz, 4H, Anth). ^{13}C {^{1}H} NMR (C_6D_6): δ (ppm) 5.41 (Si*Me*$_3$), 16.40 (CH*Me*$_2$), 28.72 (*C*H), 32.05 (*C*HMe$_2$), 123.52, 123.96, 125.09, 128.06, 129.13, 130.19, 130.50, 136.83 (Anth). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 67.57.

Preparation of [Hf{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}$_2$Cl$_2$] (Anth = 9-anthryl) (58)

A solution of [Li{CH(Pr$^i_2$P=NSiMe$_3$)(Anth)}] (**43**) prepared from the lithiation of [CH_2(Pr$^i_2$P=NSiMe$_3$)(Anth)] (**42**) (0.59g, 1.47mmol) in Et_2O (30 mL) was added

slowly to the solution of $HfCl_4$ (0.22g, 0.69mmol) in Et_2O (30 mL) at 0°C. The yellow solution was raised to ambient temperature and stirred for 12 hrs. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2. The filtrate was added with THF (*c.a.* 2mL) and concentrated to afford **58** as yellow crystals. Yield: 0.24g (15.16%). Mp: 168.0 – 172.0°C. Anal. Calcd (%) for $C_{48}H_{66}Cl_2HfN_2P_2Si_2$: C, 55.51; H, 6.41; N, 2.70; Found: C, 54.17; H, 6.38; N, 3.13. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.70 (s, 18H, Si*Me*$_3$), 0.95 (dd, J = 6.0, 9.0 Hz, 12H, CH*Me*$_2$), 1.28 (dd, J = 6.0, 9.0 Hz, 12H, CH*Me*$_2$), 1.89-1.92 (m, 4H, C*H*Me$_2$), 3.13 (d, J = 18.0 Hz, C*H*), 6.49 (t, J = 9.0 Hz, 4H, Anth), 6.90 (t, J = 9.0 Hz, 4H, Anth), 7.25 (d, J = 9.0 Hz, 4H, Anth), 7.33 (s, 2H, Anth), 7.62 (d, J = 9.0 Hz, 4H, Anth). ^{13}C {^{1}H} NMR (C_6D_6): δ (ppm) 5.56 (Si*Me*$_3$), 16.86 (CH*Me*$_2$), 28.75 (*C*H), 32.46 (*C*HMe$_2$), 123.29, 123.83, 124.27, 124.90, 129.23, 130.25, 130.40, 131.05 (Anth). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 63.80.

General Procedures for Catalytic Studies

The studies of ethylene polymerization were conducted in a 250 mL Schlenk flask. Weighed amount of precatalyst was added to a stirring solution of MAO (MAO : metal was in a ratio of approximately 1500 : 1) in toluene (50 mL) under nitrogen. After stirring for 15 minutes, the reaction mixture was degassed and then pressurized with C_2H_2 (dried with LiBu^n in hexane) at 0.5 atm. The reaction mixture was stirred for 1 h at room temperature. After that, the reaction was quenched by adding 30 mL of 10 : 1 mixture of MeOH and HCl (1 M). The polymer precipitated was then subsequently washed with water, HCl and MeOH. The polymer was then dried *in vacuo* for 2 h before weighing.

2.5 Reference for Chapter 2

1. Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1984**, *18*, 99

2. Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1

3. Sinn, H.; Kaminsky, W. Vollmer, H.-J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390

4. Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, *7*, 2375

5. Chien, J. C. W.; Sugimoto, R. *J. Polym. Sci. A, Polym. Chem.* **1991**, *29*, 459

6. Chien, J. C. W., Wang, B.-P. *J. Polym. Sci. A, Polym. Chem.* **1988**, *26*, 3089

7. Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci. A, Polym Chem.* **1990**, 28, 15

8. Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875

9. Jordan, R. F.; Bradley, P. K.; Baenzinger, N.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289

10. Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1957**, *79*, 5072.

11. Natta, G.; Pino, P.; Mazzanti, G.; Gianni, U. *J. Am. Chem. Soc.* **1957**, *79*, 2975

12. Tomaszewski, R.; Vollmerhaus, R.; Al-Humydi, A.; Wang, Q.; Taylor, N. J.; Collins, S. *Can. J. Chem.* **2006**, *84*, 214

13. Gibson, V. C.; Spitzmesser, S.K. *Chem. Rev.* **2003**, *103*, 283

14. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem. Ed. Int.* **1999**, *38*, 428

15. Tshuva E. Y.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z. *Chem. Commun.* **2000**, 379

16. Noor, A.; Kretschmer, W. P.; Glatz, G.; Meetsma, A.; Kempe, R. *Eur. J. Inorg. Chem.* **2008**, 5088

17. Lian, B.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2009**, *311*

18. Tsurugi, H.; Ohnishi, R.; Kaneko, H.; Panda, T. K.; Mashima, K. *Organometallics* **2009,** *28*, 680

19. Annunziata, L.; Pappalardo, D.; Tedesco, C.; Pellecchia, C. *Organometallics* **2009**, *28*, 688

20. Stephan, D. W.; Stewart. J. C.; Guérin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116

21. Stephan, D. W.; Guérin, F.; Spence, R. E. v. H.; Koch, L.; Gao, X.; Brown, S. J.; Swabey, J. W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics*, **1999**, *18*, 2046

22. Yue, N.; Hollink, E.; Guérin, F.; Stephan, D. W. *Organometallics* **2001**, *20*, 4424

23. Stephan, D. W.; Stewart. J. C.; Guérin, F.; Courtenay, S.; Kickham, J.; Hollink, E.; Beddie, C.; Hoskin, A.; Graham, T.; Wei, P.; Spench, R. E. v. H.; Xu, W.; Koch, L.; Gao, X.; Harrison, D. G. *Organometallics* **2003**, *22*, 1937

24. Hollink, E.; Wei, P.; Stephan, D. W. *Organometallics* **2004**, *23*, 1562

25. Beddie C.; Hollink, E.; Wei, P.; Gauld, J.; Stephan, D. W. *Organometallics* **2004**, *23*, 5240

26. Stephan, D. W. *Organometallics* **2005**, *24*, 2548

27. Ghesner, I.; Fenwich, A.; Stephan, D. W. *Organometallics* **2006**, *25*, 4985

28. Alhomaidan, O.; Bai, G.; Stephan, D. W. *Organometallics* **2008**, *27*, 6343

29. Cavell, R. G.; Kamalesh Babu, R. P.; Aparna, K.; McDonald, R. *J. Am. Chem. Soc.* **1999**, 121, 5805

30. Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **2000**, 481

31. Kamalesh Babu, R. P.; McDonald, R.; Decker, S. A.; Klobukowski, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4226

32. Cavell, R. G.; Kamalesh Babu, R. P.; Aparna, K. *J. Organomet. Chem.* **2001**, *617-618*, 158

33. Aparana, K.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Angew. Chem. Int. Ed.* **2001**, *40*, 4400

34. Sze, W.-Y. *M. Phil. Thesis, The Chinese University of Hong Kong*, **2005**

35. Wong, K.-W, *Ph. D. Thesis, The Chinese University of Hong Kong*, **2006**

36. Chan, K.-P. *M. Phil. Thesis, The Chinese University of Hong Kong*, **2007**

37. Deelman, B.-J.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Lee, H.-K.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1444

38. Wang, Z.-X.; Li, Y.-X. *Inorg. Chem.* **2002**, *41*, 5934

39. Lam, T.-W. *M. Phil. Thesis, The Chinese University of Hong Kong,* **2001**

CHAPTER 3

SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDY OF (9-ANTHRYL)(THIOPHOSPHINOYL)METHANIDE METAL COMPLEXES

3.1 Introduction

3.1.1 A General Review of Phosphoranosulfide Ligands

In chapter 1, the general aspects on the chemistry of phosphoranoimines ($R_3P{=}NR'$) have been reviewed. On the other hand, the chemistry of their analogues, phosphoranosulfides ($R_3P{=}S$), has received relatively less attention when compared to the previous one. Phosphoranosulfides have a general structure $R_3P{=}S$ with four-coordinate phosphorus and incorporating a formal phosphorus-sulphur double bond, where a highly polar P-S bond is present. Two resonance structures are allowed in phosphoranosulfides, which are the double-bonded canonical form (**I**) and the dipolar form (**II**) (**Figure 3.1**).[1]

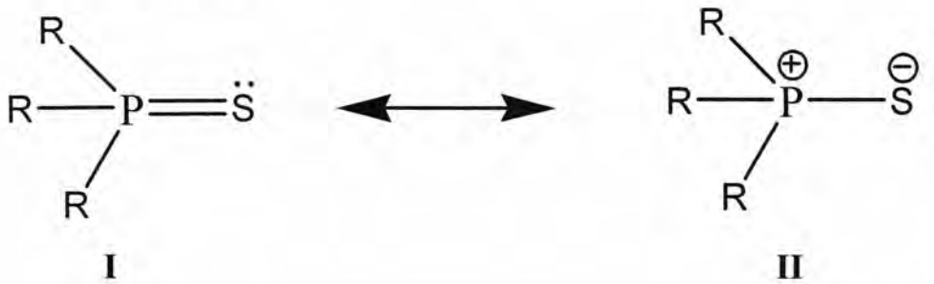
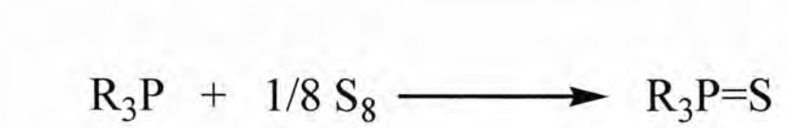


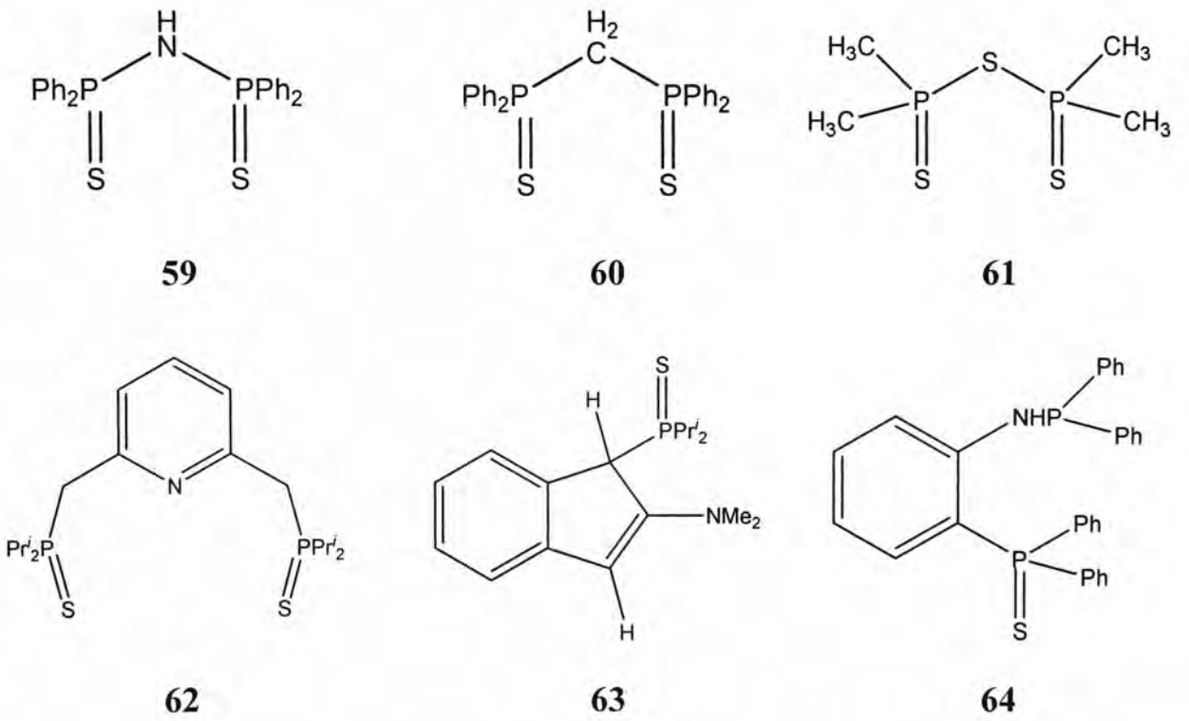
Figure 3.1

The common method of preparing phosphoranosulfides is by oxidizing corresponding phosphines with elemental sulphur (**Scheme 3.1**).[2-5]



Scheme 3.1

They usually act as monodentate or bidentate ligands in forming various metal complexes. They are sometimes incorporated with other chelating groups, e.g. nitrogen-substituted or phosphorus substituted, to become heterodifunctional ligands in order to enhance the stability of the complexes. Some selected examples of phosphanosulfide ligands (**59-64**) are shown in **Figure 3.2**.[5-10]



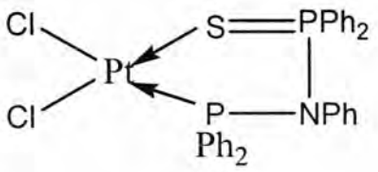
59 **60** **61**

62 **63** **64**

Figure 3.2

Phosphoranosulfides can act as neutral ligands by donating the lone pair electrons of the sulphur atom to form various metal complexes. For example, Cavell and coworkers have reported a series of transition metal complexes with bidentate

phosphane-sulfide ligand [$Ph_2PN(Ph)PPh_2$=S] (**65**), such as [{$Cl_2PtPPh_2N(Ph)P(S)Ph_2$}·H_2O] (**66**)[11]. Woollins and coworkers have also prepared several late transition metal complexes (i.e. Pt and Pd) using another phosphane-sulfide ligand [*o*-$Ph_2PNHC_6H_4P(S)Ph_2$] (**67**), e.g. *trans*-[PtMe{$Ph_2PNHC_6H_4P(S)Ph$-*P*}{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P,S*}][ClO_4](**68**)[10] (**Figure 3.3**).



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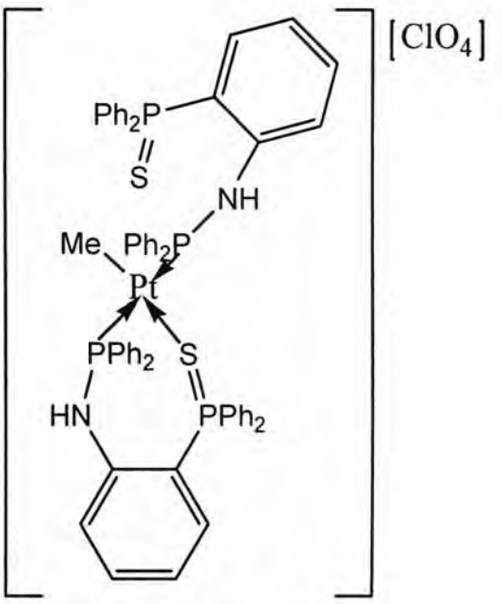

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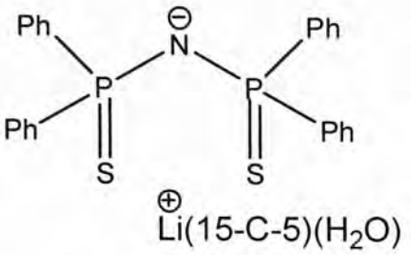
Figure 3.3

Phosphoranosulfides can be deprotonated by the organoalkali-metal or Grignard reagents to give alkali and alkali-earth metal complexes. Some alkali metal salts, for example [{Li(15-C-5)}{$Ph_2SPNPSPh_2$}·H_2O] (**69**)[12], [Na{$Ph_2P(S)NP(S)Ph_2$}(L)] [L = triglyme (**70**), tetraglyme (**71**)][13] and [{K(18-C-6)}{$Ph_2SPNPSPh_2$}] (**72**)[14] have been reported (**Figure 3.4**)



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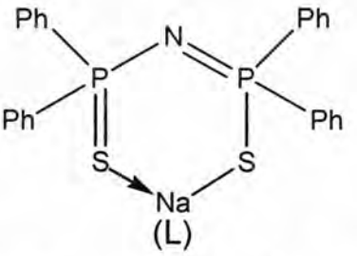
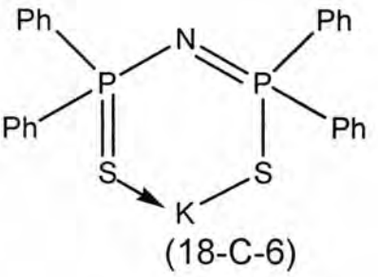


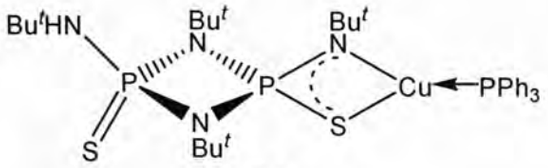
L = triglyme (**70**), tetraglyme (**71**)



72

Figure 3.4

The alkali metal salts can act as ligand transfer reagents to undergo metathesis reaction with transition and representative metals to afford various metal complexes.[15-16] For example, Chivers and coworkers have used [{(THF)$_2$Li{(^{t}BuN)(S)P(μ-N^{t}Bu)$_2$P(S)(NH^{t}Bu)}}] (**73**) as the ligand transfer reagent to synthesize a series of transition metal complexes, such as [{(PPh$_3$)Cu{(^{t}BuN)SP(μ-N^{t}Bu)$_2$PS(NH^{t}Bu)}}] (**74**) and [Pd{(^{t}BuN)(S)P(μ-N^{t}Bu)$_2$P(S)(NH^{t}Bu)}$_2$] (**75**) (**Figure 3.5**).[17] Also, Rufanov and coworkers have used [Li{(^{t}BuN)SP(NH^{t}Bu)$_2$}] (**76**) as the ligand transfer reagent to synthesize several transition metal complexes, such as [Rh(CO)$_2${(^{t}BuN)SP(NH^{t}Bu)$_2$}] (**77**) and [Ni{(^{t}BuN)SP(NH^{t}Bu)$_2$}{(^{t}BuN)$_2$P(NH^{t}Bu)(SH)}] (**78**) (**Figure 3.6**).[18]



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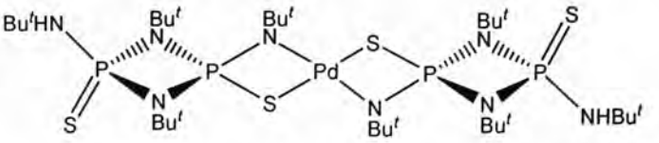
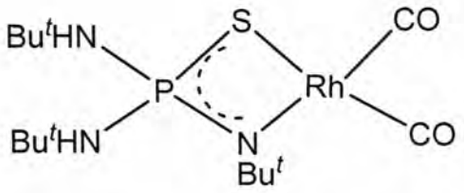


75

Figure 3.5



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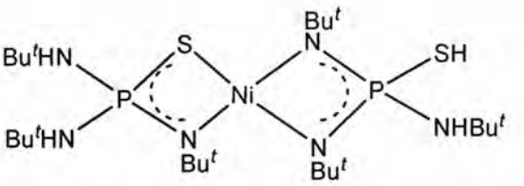
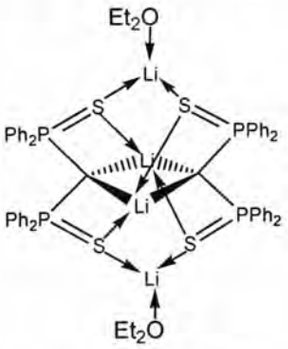


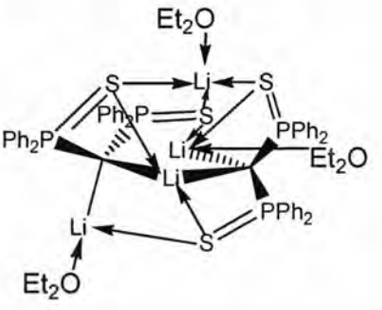
78

Figure 3.6

Previously, Mézailles and coworkers have reported the synthesis of a bis(thiophosphinoyl)-stabilized geminal dianion $[Li_2\{C(PPh_2S)_2\}]$ (**79**). It was prepared by reacting bis(thiophosphinoyl)methane with two equivalents of MeLi. Two X-ray crystal structures (**79a** and **79b**) with different solvation states were obtained for compound **79** which both exhibit a dimeric strucuture (**Figure 3.7**).[5]



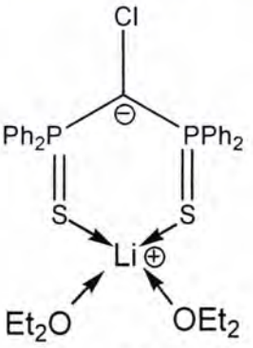
79a



79b

Figure 3.7

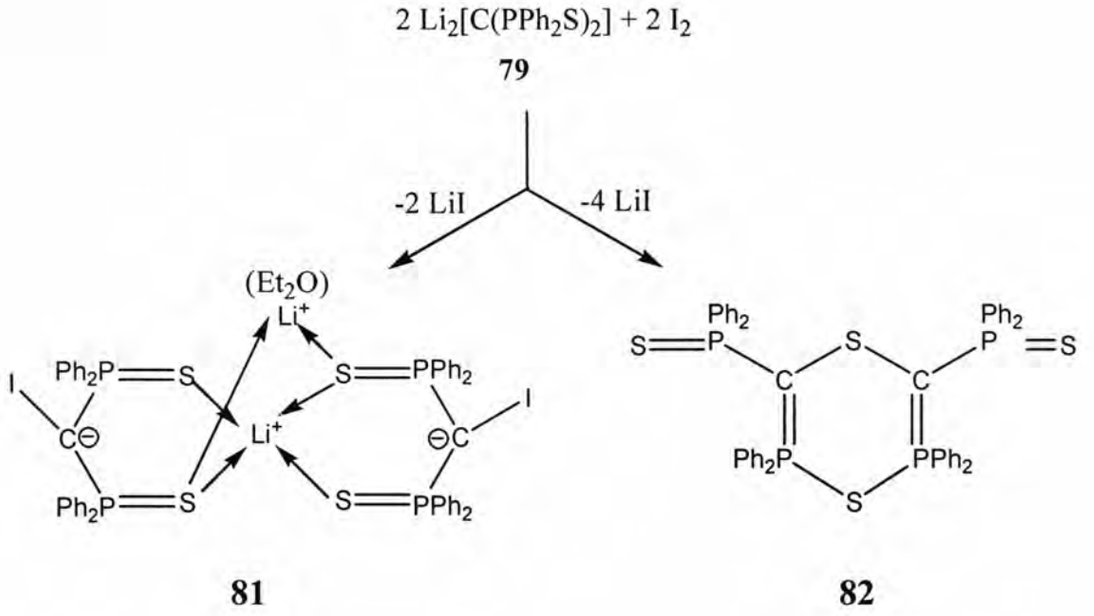
Le Floch and coworkers have reported the formation of a stable carbenoid, $[\{Li(Et_2O)_2\}\{(SPPh_2)_2CCl\}]$ (**80**) from the reaction of the dianion **79** with hexachloroethane (**Figure 3.8**). The stability of compound **80** arises from the coordination of the lithium atom by the thiophosphinoyl arms and the stabilization of the carbon lone pair in a pure *p* orbital, resulting in a strong C-Cl bond.[19]



80

Figure 3.8

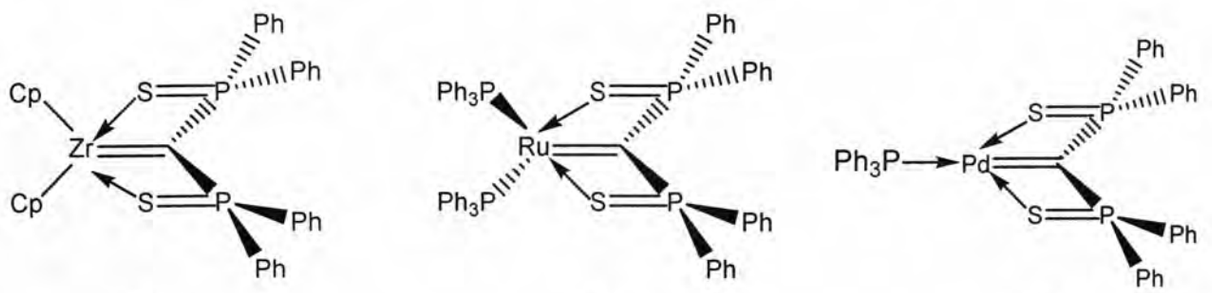
Moreover, Chivers and coworkers have reported the formation of unexpected mixture of a dimeric Li-I carbenoid $[\{(Et_2O)(\mu\text{-Li})\}\{(\mu_4\text{-Li})\{IC(PPh_2S)_2\}_2\}]$ (**81**) and a novel, unsaturated six-membered $C_2P_2S_2$ ring in $[(SPh_2P)_2C_2(PPh_2)_2S_2]$ (**82**). Compounds **81** and **82** were formed by two-electron oxidation of the dianion **79** with iodine (**Scheme 3.2**).[20]



81 **82**

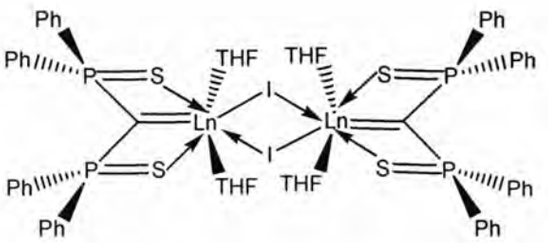
Scheme 3.2

Apart from that, the dianionic compound **79** can be treated as a S-C-S pincer ligand and used to react with corresponding metal halides to afford various transition metal and lanthanide metal carbene complexes. For example, $[Zr(Cp)_2(SPPh_2CPPh_2S)]$ (**83**)[21], $[Ru(PPh_3)_2(SPPh_2CPPh_2S)]$ (**84**)[22], $[Pd(Ph_3)(SPPh_2CPPh_2S)]$ (**85**)[23] and $[\{Ln(SPPh_2CPPh_2S)(THF)_2\}_2(\mu\text{-}I)_2]$ [Ln = Sm (**86**)[24], Tm (**87**)[25]] have been reported (**Figure 3.10**). Their chemistry has also been reviewed recently.[26]



81 **82** **83**

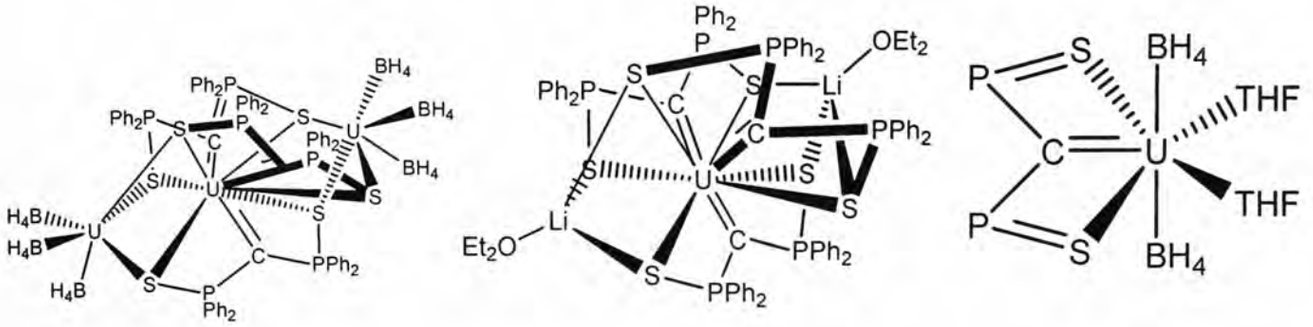
Figure 3.10



Ln = Sm (**84**), Tm (**85**)

Figure 3.10 (cont'd)

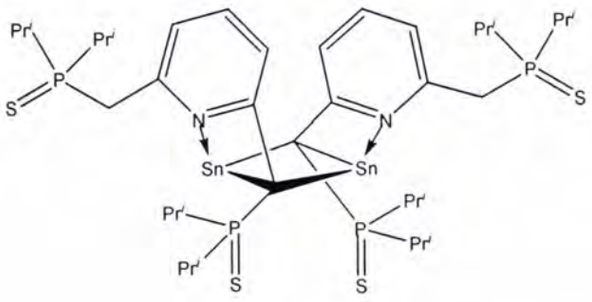
More recently, Mézailles and coworkers have successfully synthesized the first actinide carbene complexes $[U\{\mu\text{-}\{(Ph_2P{=}S)_2C\}\}_3\{U(BH_4)_3\}_2]$ (**86**) and $[U\{\mu\text{-}\{(Ph_2P{=}S)_2C\}\}_3\{Li(Et_2O)\}_2]$ (**87**). Compounds **86** and **87** were prepared by the reaction of $U(BH_4)_4$ with 1 and 3 equivalents of the dianion **79** respectively. Compound **87** can be transformed into a mononuclear derivative in THF, $[\{(Ph_2P{=}S)_2C\}U(BH_4)_2(THF)_2]$ (**88**). The structures of **86**, **87** and **88** are shown in **Figure 3.11**.[27]



86 **87** **88**

Figure 3.11

Our group is also interested in synthesizing metal complexes which contain phosphoranosulfide ligands and studying their coordination chemistry. Recently, our group has synthesized 1,3-distannacyclobutane [{2-{Sn{C(Pr^i_2P=S)}} -6-{CH_2(Pr^i_2P=S)}}C_5H_3N]$_2$ (**89**) and 1,3-diplumbacyclobutane [{2-{Pb{C(Pr^i_2P=S)}} -6-{CH_2(Pr^i_2P=S)}}C_5H_3N]$_2$ (**90**) from the reaction of neutral [(S=P$Pr^i_2CH_2$)$_2C_5H_3N$-2,6] (**62**) with one equivalent of M{$N(SiMe_3)_2$}$_2$ (M = Sn, Pb) (**Figure 3.12**).[6]



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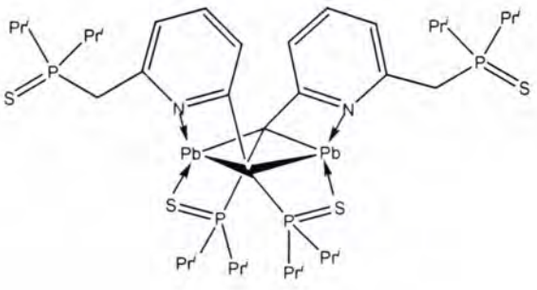


90

Figure 3.12

3.3 Objectives

The objective of the last part of this thesis aims to develop a novel phosphoranosulfide ligand using 9-anthryl group as the ligand backbone and to synthesize group 4 and 14 metal complexes by utilizing the new (9-anthryl)(thiophosphinoyl)methanide ligand (**Figure 3.13**). The metal complexes developed from this ligand are expected to be in *C,S*-chelating mode. The steric effect of the 9-anthryl group towards the structures of the complexes synthesized will be investigated.

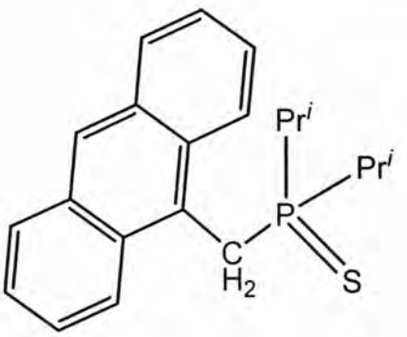


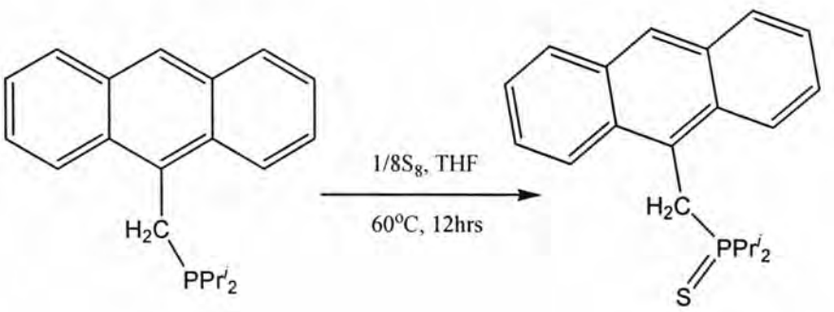
Figure 3.13

In the coming section, the monolithiated (9-anthryl)(thiophosphinoyl)methane will be synthesized. This lithium compound will be used as the ligand transfer reagent to continue synthesizing some group 4 and 14 metal complexes. Their structures will be characterized by X-ray crystallography and presented.

3.4 Results and Discussion

3.4.1.1 Synthesis of (9-Anthryl)(thiophosphinoyl)methane [$CH_2(Pr^i_2P{=}S)(Anth)$] (92) and Lithium Compound [$Li(THF)_2\{CH(Pr^i_2P{=}S)(Anth)\}$] (93)

The phosphine [$CH_2(PPr^i_2)(Anth)$] (Anth = 9-anthryl) (**91**) was prepared successfully by our group before.[1] The isolated compound **91** was allowed to react with one equivalent of elemental sulphur in THF at 60°C to afford the novel thiophosphinoyl compound, (9-anthryl)(thiophosphinoyl)methane [$CH_2(Pr^i_2P{=}S)(Anth)$] (**92**) (**Scheme 3.3**). It was isolated as pale yellow powder-like solid with the average yield of 98 %.

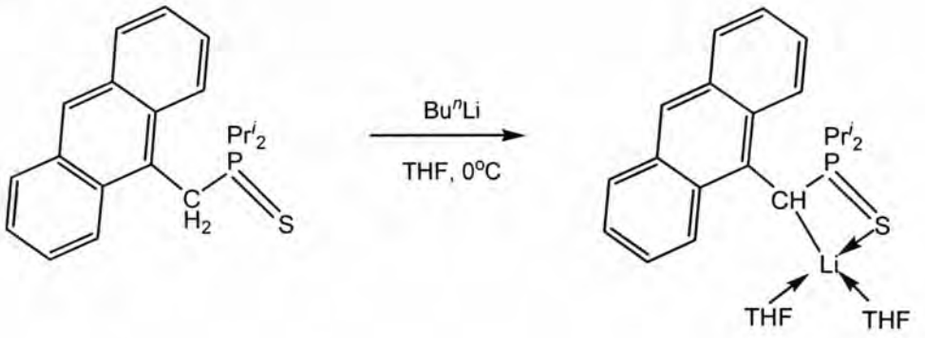


91 **92**

Scheme 3.3

The lithium complex [$Li(THF)_2\{CH(Pr^i_2P{=}S)(Anth)\}$] (**93**) was prepared by lithiation of (9-anthryl)(thiophosphinoyl)methane (**92**) with one equivalent of Bu^nLi in THF at 0°C. It was isolated as a deep purple crystalline solid with the yield of 50%

(**Scheme 3.4**).



92 **93**

Scheme 3.4

3.4.1.2 Spectroscopic Properties of 92 and 93

Compound **92** is a moisture sensitive yellow powder-like solid, while compound **93** is an extremely air and moisture sensitive deep purple crystalline solid. Both are soluble in THF, diethyl ether and toluene but only slightly soluble in hydrocarbon solvent. They were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, elemental analysis and X-ray crystallography.

The ^{1}H NMR spectra of **92** and **93** displayed signals assignable to the 9-anthryl, diisopropylphosphino and methylene protons. The 9-anthryl group displayed a set of signals in the aromatic region at δ 7.24-8.63 ppm for **92** and δ 7.26-9.18 ppm for **93**. The diisopropylphosphino group displayed two sets of double doublets at δ 0.61-0.97 ppm for **92** and δ 0.61-1.05 ppm for **93**. It also displayed one multiplet at δ 1.87-1.94 ppm for **92** and δ 2.46-2.52 ppm for **93**. The ^{1}H NMR spectrum of **92** showed a

doublet at δ 4.07 ppm (J_{P-H} = 13.2 Hz) which was due to the coupling of the methylene protons to the phosphorus nuclei, while the ^{1}H NMR spectrum of **93** showed a doublet at δ 3.74 ppm (J_{P-H} = 4.8 Hz) which was due to the coupling of methine protons to phosphorus neuclei. The ^{1}H NMR spectrum of **93** displayed peaks at δ 1.27 ppm and δ 3.74 ppm which attributed for the protons of the THF solvent molecules coordinated to the complex.

The ^{13}C NMR spectra of **92** and **93** are consistent with the solid-state structure determined. The ^{31}P NMR spectra of **92** and **93** displayed one singlet at δ 78.59 ppm and δ 78.64 ppm, respectively.

3.4.1.3 Molecular Structures of [Li(THF)$_2${CH(Pr$^i_2$P=S)(Anth)}] (93)

The molecular structure of compound **93** is shown in Figure 3.14. Selected bond distances (Å) and angles (deg) are listed in Table 3.1.

Compound **93** is a monomeric lithium complex. The lithium atom is bonded to the ligand in *C,S*-chelation fashion and coordinated to two THF solvent molecules with a distorted tetrahedral geometry. The atom is bonded to the methine carbon and sulphur atoms to form a four-membered metallacycle. The Li-S bond distance of 2.471 Å is comparable to that of 2.393(1) Å in [Li{(S=PPr$^i_2$CH)(S=PPr$^i_2$CH$_2$)C$_5$H$_3$N-2,6}(Et$_2$O)][6] and 2.457(1) Å in [(TMEDA)Li

{^{t}BuN(S)P(μ-N^{t}Bu)$_2$P(S)NH^{t}Bu}][28]. The P(1)-C(1) bond distance of 1.735(4) Å is shorter than that of 1.841 Å found in the neutral ligand, [CH_2(Pr^i_2P=S)(Anth)], while the P-S bond distance of 2.010(2) Å is longer than that of 1.954(7) Å in the ligand and 1.961(1) Å in [Ph_2P(S)(CH_2Py)][29]. It suggests that charge delocalization is likely present within the C-P-S skeleton.

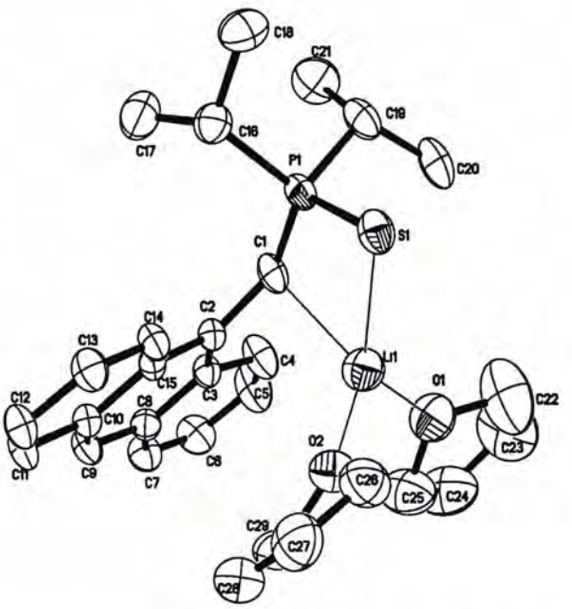


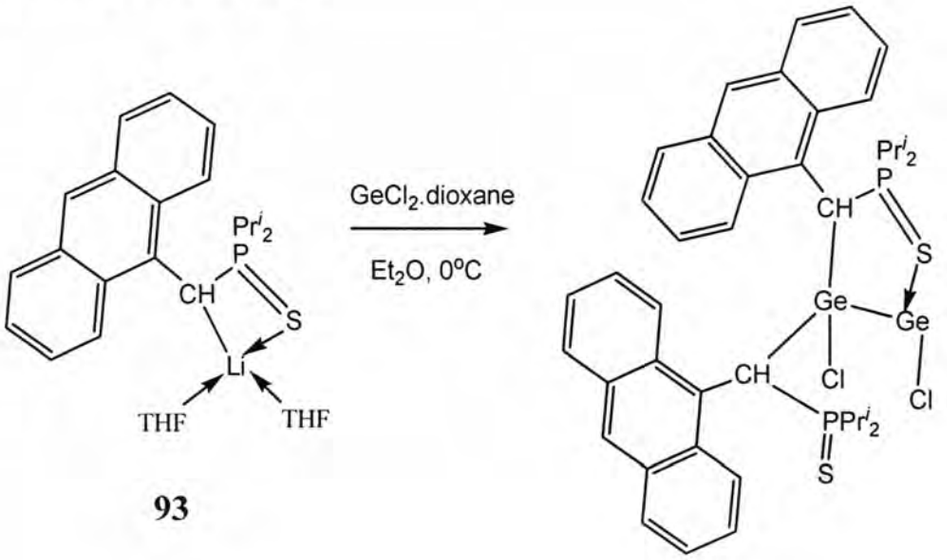
Figure 3.14 Molecular structure of [Li(THF)$_2${CH(Pr^i_2P=S)(Anth)}] (**93**).

Table 3.1 Selected bond distances (Å) and angles (deg) for compound **93**

Li(1)–C(1)	2.447(9)	Li(1)-S(1)	2.471(7)
Li(1)-P(1)	2.885(8)	P(1)-C(1)	1.735(4)
P(1)-S(1)	2.010(2)	C(1)-C(2)	1.427(4)
O(2)-Li(1)-O(1)	105.1(4)	O(2)-Li(1)-C(1)	127.7(4)
O(1)-Li(1)-C(1)	105.3(3)	O(2)-Li(1)-S(1)	107.8(3)
O(1)-Li(1)-S(1)	132.7(4)	C(1)-Li(1)-S(1)	80.0(3)
O(2)-Li(1)-P(1)	129.8(4)	O(1)-Li(1)-P(1)	124.5(4)
C(1)-Li(1)-P(1)	36.8(1)	S(1)-Li(1)-P(1)	43.2(1)
C(1)-P(1)-S(1)	114.9 (1)		

3.4.2.1 Synthesis of Germylgermylene [Ge(GeCl){CH(Pr^i_2P=S)(Anth)}$_2$Cl·2$C_6H_5CH_3$] (94)

Compound **93** reacted with one equivalent of $GeCl_2$·dioxane in diethyl ether at 0°C to give a germylgermylene complex [Ge(GeCl){CH(Pr^i_2P=S)(Anth)}$_2$Cl·2$C_6H_5CH_3$] (**94**) (**Scheme 3.5**). Compound **94** is a yellow crystalline solid with the isolated yield of 6.64%.

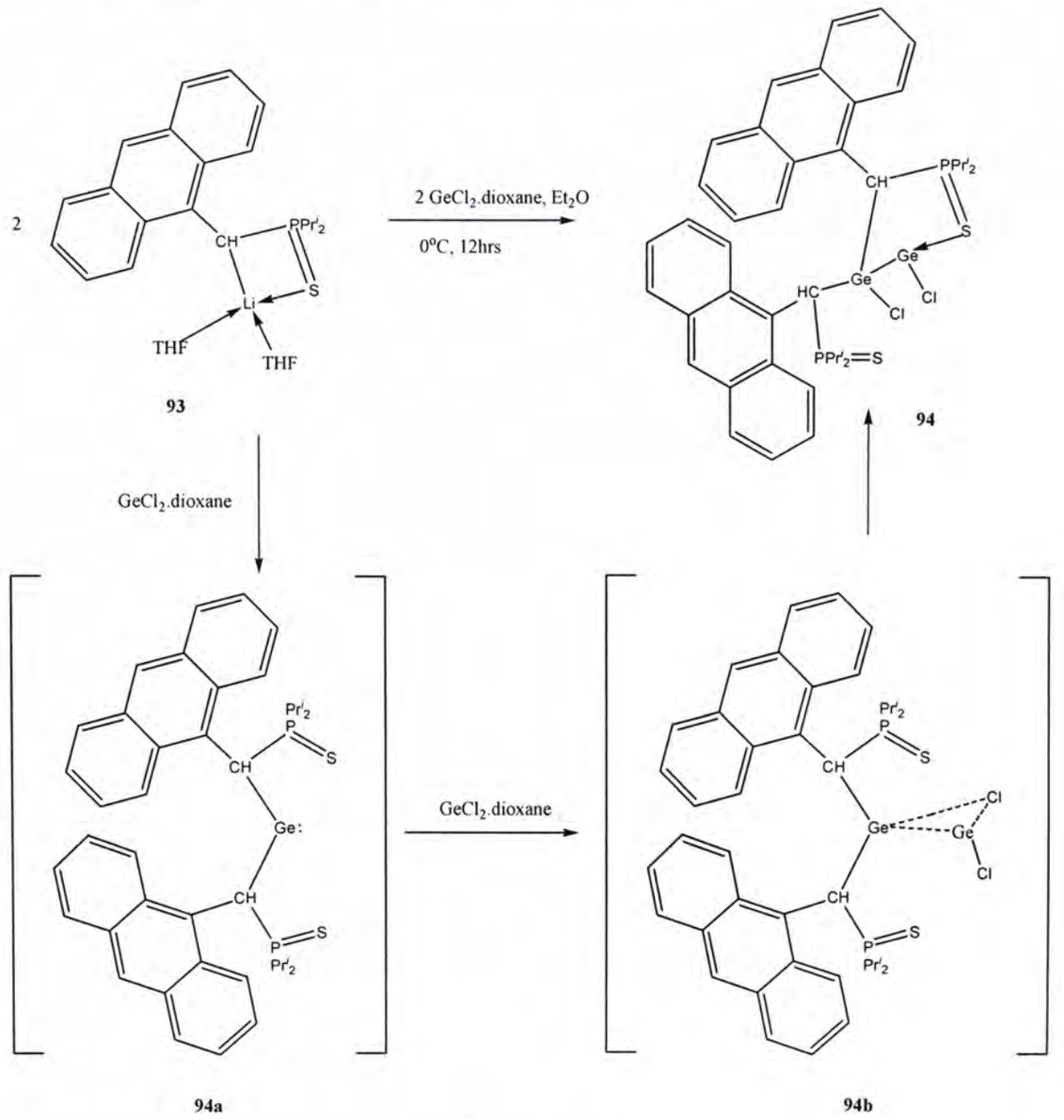


93 **94**

Scheme 3.5

It is suggested that compound **93** underwent metathesis reaction with half equivalent of $GeCl_2$ to form the homoleptic dialkylgermylene intermediate **94a**. It then underwent insertion reaction with half equivalent of $GeCl_2$ again to form the intermediate **94b** with a three-membered ring linked two germanium and one chlorine atoms together. Similar structure of the tin analogue has been reported by our group (**Figure 3.15**).[30] Subsequently, the intermediate **94b** underwent further rearrangement

to give compound **94** (**Scheme 3.6**). Similar insertion reaction of germylene into the Ge-Cl bond has been reported by Baines and coworkers before.[31]



Scheme 3.6

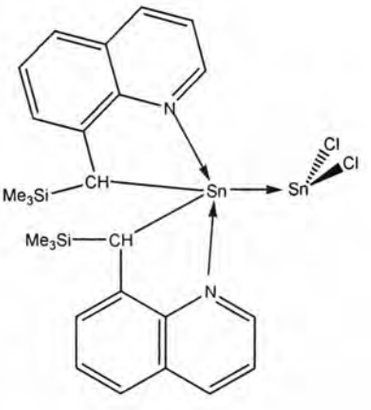


Figure 3.15

3.4.2.2 Spectroscopic Properties of 94

Compound **94** is an air and moisture sensitive yellow crystalline solid. It is soluble in THF, Et_2O and toluene but only sparingly soluble in hexane. It was characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, elemental analysis and X-ray crystallography..

The ^1H NMR and ^{13}C NMR spectra of **94** are consistent with the solid-state structure determined. It is also suggested that the two supporting ligands of the complex are homoleptic and have the same chemical environment. The ^{31}P NMR spectrum displayed one singlet signal at δ 88.30 ppm, which also supports that the two phosphorus atoms are in the same chemical environment.

3.4.2.3 Molecular Structure of $[Ge(GeCl)\{CH(Pr^i_2P{=}S)(Anth)\}_2Cl{\cdot}2C_6H_5CH_3]$ (94)

The molecular structure of compound **94** is shown in Figure 3.16. Selected bond distances (Å) and angles (deg) are listed in Table 3.2.

Compound **94** is a monomeric germylgermylene complex with a distorted tetrahedral geometry about the four-coordinate tetravalent germanium atom, featuring a Ge^{II}-Ge^{IV} bonding. In the cyclic digermylene, the germanium(IV) center is bonded to the germanium(II) atom and a ligand backbone, forming a five-membered

metallacycle. The average Ge^{IV}-C bond distance of 2.044 Å is slightly longer than that of 2.005 Å in $[Ge\{GeCl_2\{(S=PPr^i_2CH)(S=PPr^i_2CH_2)C_5H_3N\text{-}2,6\}\}_2]$[6] and that of 1.924(7) Å in $[\{Ge\{C(C_5H_4N\text{-}2)C(Ph)N(SiMe_3)\}Cl_2\}_2]$[32]. It may be due to the steric effect between the two ligands. The Ge(II) and Ge(IV) atoms are bound by a single bond with the bond distance of 2.540(2) Å. It is comparable to that of 2.544(7) Å in $[C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2GeGe(Bu^t)_3]$[33] but is slightly longer than that of 2.480 Å in $[Ge\{GeCl_2\{(S=PPr^i_2CH)(S=PPr^i_2CH_2)C_5H_3N\text{-}2,6\}\}_2]$[6] and 2.449(1) Å in $[\{\{\mu\text{-}(Me_3Si)C(PMe_2)_2\}_2Ge_2\}_2GeCl_2]$[34]. The Ge(2)-S bond distance of 2.468(3) Å is significantly shorter than that of 2.675(1) Å in $[Ge\{GeCl_2\{(S=PPr^i_2CH)(S=PPr^i_2CH_2)C_5H_3N\text{-}2,6\}\}_2]$[6]. The average P-C bond distance of 1.845 Å is in good agreement with that of 1.841 Å found in the neutral ligand, $[CH_2(Pr^i_2P=S)(Anth)]$, while the P-S bond distance of 1.999 Å is longer than the P=S bond distance of 1.954(7) Å in the ligand and 1.961(1) Å in $[Ph_2P(S)(CH_2Py)]$[29].

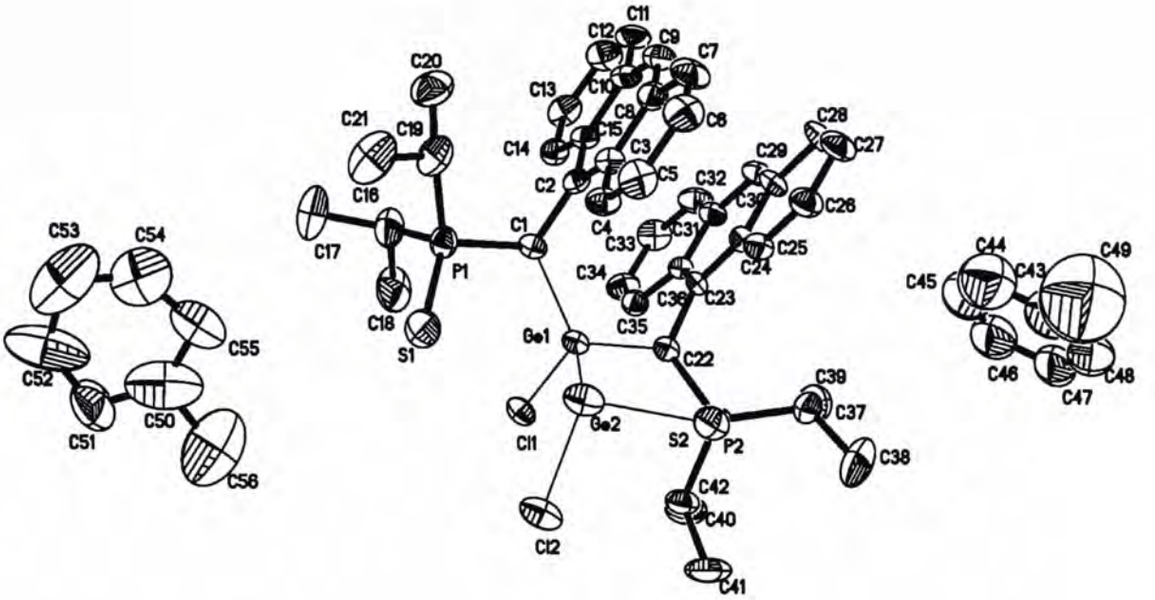


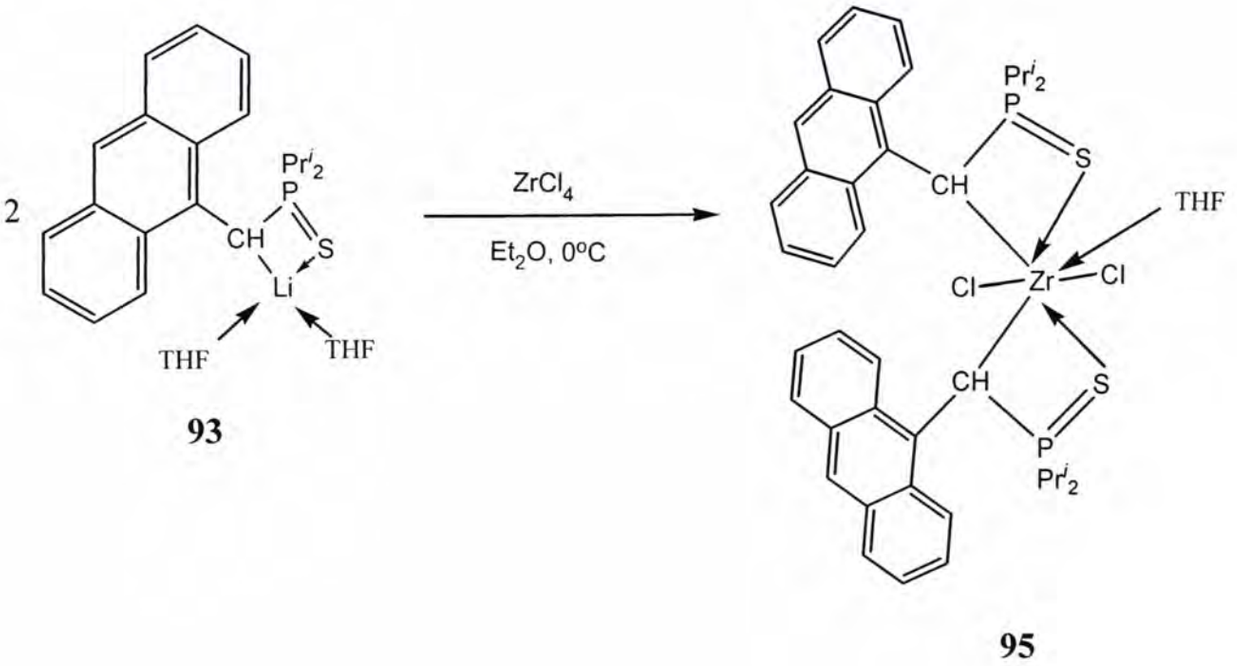
Figure 3.16 Molecular structure of $[Ge(GeCl)\{CH(Pr^{i}_{2}P{=}S)(Anth)\}_{2}Cl{\cdot}2C_{6}H_{5}CH_{3}]$ (**94**).

Table 3.2 Selected bond distances (Å) and angles (deg) for compound **94**

Ge(1)-C(1)	2.028(8)	Ge(1)-C(22)	2.059(8)
Ge(1)-Cl(1)	2..228(2)	Ge(1)-Ge(2)	2.540(2)
Ge(2)-Cl(2)	2.267(3)	Ge(2)-S(2)	2.468(3)
P(1)-C(1)	1.877(8)	P(1)-S(1)	1.941(4)
P(2)-C(22)	1.812(8)	P(2)-S(2)	2.057(4)
C(1)-Ge(1)-C(22)	108.7(3)	C(1)-Ge(1)-Cl(1)	100.8(2)
C(22)-Ge(1)-Cl(1)	95.5(3)	C(1)-Ge(1)-Ge(2)	124.5(2)
C(22)-Ge(1)-Ge(2)	110.9(2)	Cl(1)-Ge(1)-Ge(2)	112.3(8)
Cl(2)-Ge(2)-S(2)	98.2(2)	Cl(2)-Ge(2)-Ge(1)	96.7(8)
S(2)-Ge(2)-Ge(1)	87.4(7)	P(2)-C(22)-Ge(1)	107.8(4)
P(2)-S(2)-Ge(2)	107.4(1)		

3.4.3.1 Synthesis of (9-Anthryl)(thiophosphinoyl)methanide Zirconium(IV) Complex [Zr{CH(Pr$^i_2$P=S)(Anth)}$_2$Cl$_2$(THF)·THF] (95)

The lithium complex **93** underwent metathesis reaction with $ZrCl_4$ in a 2 : 1 ratio in diethyl ether at 0°C to give zirconium(IV) complex [Zr{CH(Pr$^i_2$P=S)(Anth)}$_2$Cl$_2$(THF)·THF] (**95**) (**Scheme 3.7**). The isolated yield of **95** was 19.36%.



93 **95**

Scheme 3.7

3.4.3.2 Spectroscopic Properties of 95

Compound **95** is an air and moisture sensitive yellow crystalline solid. It is soluble in THF and CH_2Cl_2 but only slightly soluble in hexane. It has been characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, elemental analysis and X-ray crystallography.

The ^{1}H NMR spectrum of **95** displayed two multiplets at δ 1.38 ppm and δ 3.77 ppm for the protons of the coordinated THF molecule. The ^{13}C NMR spectrum of **95** is also consistent with the solid-state structure. Only one set of signals was observed in both the ^{1}H and ^{13}C spectra, suggesting that the two supporting ligands are homoleptic and have the same chemical environment. The ^{31}P NMR spectrum of **95** showed a singlet at δ 85.70 ppm which can be deduced that the two phosphorus atoms are in the same chemical environment.

3.4.3.3 Molecular Structure of [Zr{CH(Pr$^{i}_{2}$P=S)(Anth)}$_2$Cl$_2$(THF)·THF] (95)

The molecular structure of compound **95** is shown in Figure 3.17. Selected bond distances (Å) and angles (deg) are listed in Table 3.3.

Compound **95** is a monomeric dichlorozirconium(IV) compound. The metal center of **95** is bonded to two chloride ligands and coordinated to two ligands in *C,S*-chelation fashion forming two four-membered metallacycles. In addition, it is coordinated to a THF solvent molecule. It has a pentagonal bipyramidal geometry about the metal center.

The average Zr-Cl distance of 2.455 Å is similar to those of 2.513 Å in [Zr{N(SiMe$_3$)C(Bu^{t})C(H)(C$_5$H$_4$N-2)}$_2$Cl$_2$][35], 2.442Å in [ZrCl$_2${CH(Ph$_2$P=NSiMe$_3$)(C$_6$H$_5$)}$_2$][36] and 2.445Å in [Zr{P(Ph)C(=CHPh)P(Me)$_2$=NSiMe$_3$}$_2$Cl$_2$][37]. The average

P-C(methine) distance of 1.751 Å is shorter than that of 1.841(2) Å in the neutral ligand, $[CH_2(Pr^i_2P{=}S)(Anth)]$, and the average P-S distance of 2.006 Å is longer than that of 1.953(7) Å in the ligand and 1.961(1) Å in $[Ph_2P(S)(CH_2Py)]$[29]. It suggests that charge delocalization is likely present within the C-P-S skeleton.

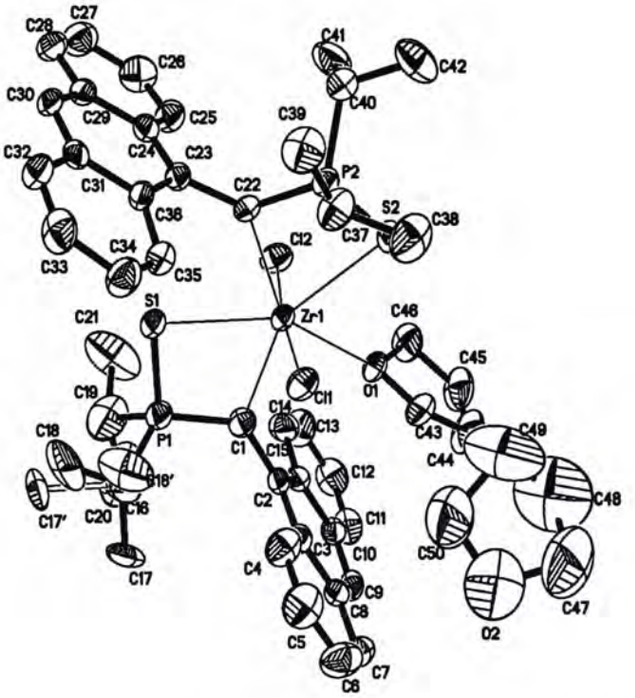


Figure 3.17 Molecular structure of $[Zr\{CH(Pr^i_2P{=}S)(Anth)\}_2Cl_2(THF)\cdot THF]$ (**95**).

Table 3.3 Selected bond distances (Å) and angles (deg) for compound **95**

Zr(1)-O(1)	2.303(4)	Zr(1)-C(22)	2.436(6)
Zr(1)-Cl(1)	2.443(2)	Zr(1)-C(1)	2.451(7)
Zr(1)-Cl(2)	2.466(2)	Zr(1)-S(1)	2.593(2)
Zr(1)-S(2)	2.695(2)	S(1)-P(1)	2.007(3)
S(2)-P(2)	2.005(3)	P(1)-C(1)	1.714(7)
P(2)-C(22)	1.788(1)		
C(22)-Zr(1)-Cl(1)	93.2(2)	C(22)-Zr(1)-C(1)	143.3(2)
Cl(1)-Zr(1)-C(1)	89.4(2)	C(22)-Zr(1)-Cl(2)	89.7(2)
Cl(1)-Zr(1)-Cl(2)	174.1(7)	C(1)-Zr(1)-Cl(2)	91.4(2)
C(22)-Zr(1)-S(1)	69.3(2)	Cl(2)-Zr(1)-S(1)	90.7(7)
C(22)-Zr(1)-S(2)	68.1(2)	Cl(1)-Zr(1)-S(2)	86.1(7)
C(1)-Zr(1)-S(2)	148.5(2)	Cl(2)-Zr(1)-S(2)	90.2(7)
S(1)-Zr(1)-S(2)	142.2(6)		

3.4.3.4 Catalytic Study of [Zr{CH(Pr^i_2P=S)(Anth)}$_2$Cl$_2$(THF)·THF] (95)

The catalytic activity of compound **95** towards ethylene polymerization was studied and the result is shown in Table 3.4.

Table 3.4 Catalytic activity of compound **95** on ethylene polymerization

compound (precatalyst)	amount of precatalyst used (μmol)	PE yield (g)	activity ($gmmol^{-1}h^{-1}$)
95	19.6	1.65	84.2
Cp_2ZrCl_2	32.8	3.90	118.9

The catalytic activity of compound **95** towards ethylene polymerization was found to be 84.2 $gmmol^{-1}h^{-1}$. It is comparable to that of 92.49 $gmmol^{-1}h^{-1}$ of $[ZrCl_2\{CH(Ph_2P{=}NSiMe_3)(C_6H_5)\}_2]$[36], which showed high catalytic activity on ethylene polymerization. The two highly conjugated systems in Zr-C-P-S rings present in compound **95** can be accounted for the high catalytic activity. The structural characteristic of conjugated system is similar to the conventional zirconocene dichloride complex $[Cp_2ZrCl_2]$. However, the activity is still lower than the reported literature values for $[Cp_2ZrCl_2]$ under similar experimental conditions.[38, 39]

3.5 Experimental Section

Materials: LiBu^n, 9-anthracarboxaldehyde, lithium wire, chlorodiisopropylphosphine, elemental sulphur, $GeCl_2$·dioxane and $ZrCl_4$ were purchased from Aldrich Chemical Co. and used without further purification.

Preparation of [$CH_2(Pr^i_2P{=}S)(Anth)$] (Anth = 9-anthryl) (92)

A solution of [$CH_2(PPr^i_2)(Anth)$] (**91**) (0.27g, 0.68mmol) in THF (30mL) was added slowly to the solution of sulphur (0.20g, 0.87mmol) in THF (30mL) at room temperature. The reaction mixture was stirred at 60°C for 12 hrs. The volatiles were removed under reduced pressure and compound **92** was obtained as pale yellow solid. Yield: 0.23g (98%). Mp: 191.6 - 193.6 °C. Anal. Calcd (%) for $C_{21}H_{25}PS$: C, 74.09; H, 7.40; N, 0.00; Found: C, 71.50; H, 7.19; N, <0.10. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.61 (dd, J = 7.2, 9.6 Hz, 6H, CH*Me*$_2$), 0.89 (dd, J = 6.9, 9.5 Hz, 6H, CH*Me*$_2$), 1.87-1.94 (m, 2H, C*H*Me$_2$), 4.07 (d, J = 13.2 Hz, C*H*$_2$), 7.24 (t, J = 7.3 Hz, 2H, Anth), 7.40 (t, J = 7.8 Hz, 2H, Anth), 7.78 (d, J = 8.5 Hz, 2H, Anth), 8.13 (s, 1H, Anth), 8.60 (d, J = 9.0 Hz, 2H, Anth). ^{13}C {^{1}H} NMR (C_6D_6): δ (ppm) 1.76 (CH*Me*$_2$), 17.00 (*C*H), 29.18 (*C*HMe$_2$), 125.77, 126.34, 126.59, 126.87, 129.74, 131.69, 132.46, 132.50 (Anth). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 78.59.

Preparation of [$Li(THF)_2${$CH(Pr^i_2P{=}S)(Anth)$}] (Anth = 9-anthryl) (93)

To a solution of **92** (0.35g, 0.90mmol) in THF (30mL), ^{n}BuLi (0.56mL, 0.90mmol) was added slowly at 0°C. The reaction mixture was stirred at room temperature for 12 hrs and a dark green solution was formed. The volatiles were removed under reduced pressure and the residue was extracted with Et_2O. After filtration and concentration, compound **93** was obtained as purple crystals. Yield: 0.22g (50.0%). Mp: 168.0 –

172.0°C. Anal. Calcd (%) for $C_{21}H_{24}LiPS\cdot 2THF$: C, 71.00; H, 8.22; N, 0.00; Found: C, 59.69; H, 6.55; N, <0.10. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.60 (dd, J = 7.2, 9.6 Hz, 6H, CHMe_2), 0.90 (dd, J = 6.9, 9.5 Hz, 6H, CHMe_2), 1.27 (m, 8H, THF) 2.46-2.52 (m, 2H, CHMe$_2$), 3.74 (m, 8H, THF), 4.05 (d, J = 4.8 Hz, CH), 7.26 (t, J = 7.3 Hz, 2H, Anth), 7.26 (t, J = 7.8 Hz, 2H, Anth), 7.78 (d, J = 8.5 Hz, 2H, Anth), 8.59 (s, 1H, Anth), 9.15 (d, J = 9.0 Hz, 2H, Anth). ^{13}C {^{1}H} NMR (C_6D_6): δ (ppm) 1.75 (CHMe_2), 16.98 (CH), 25.44 (THF), 29.17 (CHMe$_2$), 66.26 (THF), 121.76, 125.47, 125.77, 126.35, 129.73, 131.75, 132.45, 134.59 (Anth). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 78.64.

Preparation of [Ge(GeCl){CH(Pr^i_2P=S)(Anth)}$_2$Cl$\cdot$2$C_6H_5CH_3$] (Anth = 9-anthryl) (94)

A solution of [Li(THF)$_2${CH(Pr^i_2P=S)(Ar)}] (**93**) (0.34g, 0.69mmol) in Et_2O (30mL) was added slowly to the solution of $GeCl_2\cdot$dioxane (0.17g, 0.73mmol) in Et_2O (30mL) at 0°C. The yellow solution was raised to ambient temperature and stirred for 12 hrs. The volatiles were removed under reduced pressure and the residue was extracted with toluene. The yellow mixture was filtered and concentrated, yellow crystals of title compounds were obtained. Yield: 0.05g (6.64%). Mp: 294.1 – 298.5°C. Anal. Calcd (%) for $C_{42}H_{64}Cl_2Ge_2P_2S_2\cdot 2C_6H_5CH_3$: C, 62.32; H, 5.98; N, 0.00; Found: C, 61.00; H, 5.96; N, <0.10. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.58 (dd, J = 7.2, 9.6 Hz, 6H, CHMe_2), 0.87 (dd, J = 6.9, 9.5 Hz, 6H, CHMe_2), 2.11 (s, 6H, $C_6H_5CH_3$), 2.32-2.37 (m, 2H, CHMe$_2$), 4.81 (d, J = 9.0 Hz, CH), 7.02, 7.12 (m, 10H, $C_6H_5CH_3$) 7.26 (t, J = 7.3 Hz, 2H, Anth), 7.31 (t, J = 7.8 Hz, 2H, Anth), 8.00 (d, J = 8.5 Hz, 2H, Anth), 8.15 (s, 1H, Anth), 8.24 (d, J = 9.0 Hz, 2H, Anth). ^{13}C {^{1}H} NMR (C_6D_6): δ (ppm) 1.75 (CHMe_2), 2.79 (CH), 20.71 ($C_6H_5CH_3$) 90.14 (CHMe$_2$), 125.97, 128.06, 129.10, 131.19 ($C_6H_5CH_3$), 126.29, 126.61, 127.02, 127.34, 127.66, 130.15, 130.47,

130.79 (Anth). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 88.30.

Preparation of [Zr{CH(Pr$^{i}_{2}$P=S)(Anth)}$_2$Cl$_2$(THF)·THF] (Anth = 9-anthryl) (95)

A solution of [Li(THF)$_2${CH(Pr$^{i}_{2}$P=S)(Ar)}] (**93**) (0.79g, 1.57mmol) in Et_2O (30mL) was added slowly to the solution of $ZrCl_4$ (0.19g, 0.79mmol) in Et_2O (30mL) at 0°C. The yellow solution was raised to ambient temperature and stirred for 12 hrs. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2. The filtrate was added with THF (*c.a.* 2mL) and concentrated to afford **95** as yellow crystals. Yield: 0.16g (19.36%). Mp: 294.1 – 298.5°C. Anal. Calcd (%) for $C_{46}H_{56}Cl_2OP_2S_2Zr$·THF: C, 60.96; H, 6.55; N, 0.00; Found: C, 59.77; H, 6.13; N, N/A. ^{1}H NMR (300MHz, C_6D_6): δ (ppm) 0.63 (dd, J = 7.2, 9.6 Hz, 6H, CH*Me$_2$*), 0.91 (dd, J = 6.9, 9.5 Hz, 6H, CH*Me$_2$*), 1.38 (m, 8H, THF), 1.87-1.94 (m, 2H, C*H*Me$_2$), 3.77 (m, 8H, THF), 4.06 (d, J = 12.0 Hz, C*H*), .26 (t, J = 7.3 Hz, 2H, Anth), 7.46 (t, J = 7.8 Hz, 2H, Anth), 7.79 (d, J = 8.5 Hz, 2H, Anth), 8.61 (s, 1H, Anth), 9.15 (d, J = 9.0 Hz, 2H, Anth). ^{13}C $\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 1.75 (CH*Me$_2$*), 17.00 (*C*H), 19.09 (*C*HMe$_2$), 25.60, 70.07 (THF), 123.57, 124.75, 125.30, 125.83, 130.22, 131.65, 132.65, 133.01 (Anth). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ (ppm) 85.70.

3.6 Reference for Chapter 3

1. Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982
2. Bereman, R. D.; Wang, F. T.; Najdzionek, J.; Braitsch, D.M. *J. Am. Chem. Soc.* **1976**, *98*, 7266
3. Wang, F. T.; Najdzionek, J.; Leneker, K. L.; Wasserman, H.; Braitsch, D. M. *Synth. React. Inorg. Met. Org. Chem.* **1978**, *8*, 119
4. Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans*. **1995**, 2489
5. Cantat, T.; Ricard, L.; Le Floch, P.; Mézailles, N. *Organometallics*, **2006**, *25*, 4965
6. Kan, K.-W. *Ph D. Thesis, The Chinese University of Hong Kong*, **2007**
7. Schmidpeter, A.; Böhm, R.; Groeger, H. *Angew. Chem.* **1964**, *76*, 860
8. Wheatland, D. A.; Clapp, C. H.; Waldron, R. W. *Inorg. Chem*. **1972**, *11*, 2340
9. Wechsler, D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Chem Commun.* **2004**, 2446
10. Aucott, S. M.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2002**, 2408
11. Balahkrishna, M. S.; Klein, R.; Uhlenbrock, S.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 5676
12. Hernández-Arganis, M.; Hernández-Orterga, S.; Toscano, R. A.;

García-Montalvo, V.; Cea-Olivares, R. *Chem. Commun.* **2004**, 310

13. Blake, A. J.; Darr, J. A.; Howdle, S. M.; Poliakoff, M.; Li, W.-S.; Webb, P. B. *J. Chem. Crystallogr.* **1999**, *29*, 547

14. Cea-Olivares, R.; Nöth, H. *Z. Naturforsch.* **1987**, *42b*, 1507

15. Silvestru, C.; Drake, J. E. *Coord. Chem. Rev.* **2001**, *223*, 117

16. Bhattacharyya, P.; Woollins, J. D. *Polyhedron* **1995**, *23-24*, 3367

17. Chivers, T.; Fedorchuk, C.; Krahn, M.; Parvez, M. ; Schatte, G. *Inorg. Chem.* **2001**, *40*, 1936

18. Rufanov, K. A.; Ziemer, B.; Meisel, M. *Dalton Trans.* **2004**, 3808

19. Cantat, T.; Jacques, X.; Ricard, L.; Le Goff, X. F. ; Mézailles, N.; Le Floch, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 5947

20. Konu, J.; Chivers, T. *Chem. Commun.* **2008**, 4995

21. Cantat, T.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2006**, *25*, 6030

22. Cantat, T.; Demange, M.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Organometallics* **2005**, *24*, 4838

23. Cantat, T.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 6382

24. Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Le Floch, P. *Chem.*

Commun. **2005**, 5178

25. Cantat, T.; Jaroschik, F.; Ricard, L.; Le Floch, P.; Nief, F.; Mézailles, N. *Organometallics* **2006**, *25*, 1329
26. Cantat, T.; Mézailles, N.; Auffrant, A.; Le Floch, P. *Dalton Trans.* **2008**, 1957
27. Cantat, T.; Arliguie, T.; Noel, A.; Thuery, P.; Ephritikhine, M.; Le Floch, P.; Mézailles, N. *J. Am. Chem. Soc.* **2009**, *131*, 963
28. Chivers, T.; Krahn. M.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 2547
29. Kling, C.; Ott, H.; Schwab, G.; Stalke, D. *Organometallics* **2008**, *27*, 5038
30. Leung, W.-P.; Kwok, W.-H.; Xue, F.; Mak, T. C. W. *J. Am. Chem. Soc.* **1997**, *119*, 1145
31. Rupar, P. A.; Jennings, M. C.; Baines, K. M. *Organometallics*, **2008**, *27*, 5043
32. Leung, W.-P.; So, C.-W.; Wu, Y.-Z.; Li, H.-W.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2005**, *513*
33. Seteka, W.; Sakamoto, K.; Kira, M.; Power, P. P. *Organometallics* **2001**, *20*, 4460
34. Karsh, H. H.; Deubelly, B.; Riede, J.; Müller, G. *Angew. Chem. Int. Ed.* **1987**, *26*, 674
35. Deelman, B.-J.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Lee, H.-K.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1444
36. Wong, K.-W. *Ph. D. Thesis, The Chinese University of Hong Kong*, **2006**

37. Wang, Z.-X.; Li, Y.-X. *Inorg. Chem.* **2002**, *41*, 5934

38. Hollink, E.; Wei, P.; Stephan, D. W. *Can. J. Chem.* **2004**, *82*, 1304

39. Möhring, P. C.; Coville, J. C. *J. Organomet. Chem.* **1994**, *479*, 1

Appendix I

A. General Procedures

All experiments were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over and freshly distilled, under nitrogen, from CaH_2 (hexane), sodium benzophenone ketyl (Et_2O, THF), sodium/potassium alloy (pentane, toluene) and degassed three times by freeze-thaw cycle prior to use.

B. Physical and Analytical Measurements

(i) *Spectroscopic Measurements*

^1H NMR spectra were recorded at 300.13 MHz using a Bruker DPX-300 spectrometer. Chemical shifts were referenced to δ 7.16 ppm for C_6D_6 and δ 7.26 ppm for $CDCl_3$.

$^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 MHz, using a Bruker DPX-300 spectrometer. Chemical shifts were referenced to δ 128.00 ppm for C_6D_6.

$^{31}P\{^1H\}$ NMR spectra were recorded at 121.49 MHz using a Bruker DPX-300 spectrometer. Chemical shifts were referenced to δ 0.00 ppm for 0.0485 M Triphenyl Phosphate in $CDCl_3$.

$^{119}Sn\{^{1}H\}$ NMR spectra were recorded at 149.14 MHz using an INOVA Varian 400 spectrometer. Chemical shifts were referenced to δ 0.00 ppm for external $SnMe_4$.

(ii) *Microanalysis*

Elemental (C, H, N) analysis was performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, Middlesex, U.K.

(iii) *Melting Point Measurements*

Melting points were recorded on an Electrochemical Melting Point Apparatus and were uncorrected.

Appendix II

Table A.1. Selected Crystallographic Data for Compounds 44-46

	44	**45**	**46**
Formula	$C_{24}H_{33}ClGeNPSi$	$C_{24}H_{33}ClNPSiSn$	$C_{48}H_{66}N_2P_2Si_2Sn$
Fw	502.61	548.71	907.84
Color	Yellow	Yellow	Orange
cryst syst	Monoclinic	Monoclinic	Orthorhombic
space group	$P2_1/n$	$P2_1/n$	Pbca
a (Å)	8.635(3)	8.769(2)	21.271(4)
b (Å)	18.809(3)	18.695(5)	17.965(3)
c (Å)	15.761(3)	15.930(4)	24.938(4)
α (deg)	90.00	90.00	90.00
β (deg)	97.50(1)	97.33(2)	90.00
γ (deg)	90.00	90.00	90.00
V (Å^3)	2538.0(8)	2590.6(11)	9530(3)
Z	4	4	8
d_{calcd} (g cm^{-3})	1.315	1.407	1.266
μ (mm^{-1})	1.433	1.208	0.687
F(000)	1048	1120	3808
cryst size (mm)	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30
2θ range (deg)	1.69-28.07	1.69-28.09	1.63-25.00
index range	$-11 \le h \le 8$,	$-11 \le h \le 11$,	$-25 \le h \le 23$,
	$-24 \le k \le 24$,	$-22 \le k \le 24$,	$-21 \le k \le 21$,
	$-18 \le l \le 20$	$-20 \le l \le 21$	$-29 \le l \le 24$
no. of rflns collected	17215	17386	49350
no. of indep rflns	6148	6278	8387
R1, wR2 ($I > 2(\sigma)I$)	0.0675, 0.1698	0.0410, 0.1077	0.0686, 0.1696
R1, wR2 (all data)	0.1548, 0.2197	0.0540, 0.1146	0.1422, 0.2437
goodness of fit, F^2	1.004	1.061	1.098
no. of data/restraints/params	6148/0/262	6278/0/262	8387/0/496
largest diff peaks, eÅ^{-3}	1.664 to –0.530	1.219 to –0.828	0.925 to –0.977

Table A.2. Selected Crystallographic Data for Compounds 57, 58 and 93

	57	58	93
Formula	$C_{48}H_{66}Cl_2N_2P_2Si_2Zr$	$C_{48}H_{66}Cl_2HfN_2P_2Si_2$	$C_{29}H_{40}LiO_2PS$
Fw	951.27	1038.54	490.58
Color	Yellow	Yellow	Purple
cryst syst	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/c$	P1
a (Å)	19.365(8)	19.439(3)	8.382(3)
b (Å)	13.110(6)	13.150(2)	10.090(4)
c (Å)	19.916(8)	19.964(3)	17.984(7)
α (deg)	90.00	90.00	97.070(6)
β (deg)	109.656(8)	109.644(2)	102.675(6)
γ (deg)	90.00	90.00	107.851(7)
V (Å^3)	4762(4)	4806.1(14)	1382.6(9)
Z	4	4	2
d_{calcd} (g cm^{-3})	1.327	1.435	1.178
μ (mm^{-1})	0.495	2.433	0.198
F(000)	2000	2128	528
cryst size (mm)	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30
2θ range (deg)	1.12-25.00	1.11-25.00	2.17-25.00
index range	$-23 \le h \le 20$,	$-23 \le h \le 23$,	$-9 \le h \le 9$,
	$-15 \le k \le 15$,	$-15 \le k \le 8$,	$-11 \le k \le 11$,
	$-23 \le l \le 22$	$-21 \le l \le 23$	$-21 \le l \le 21$
no. of rflns collected	25508	25110	7536
no. of indep rflns	8378	8457	4824
R1, wR2 ($I > 2(\sigma)I$)	0.0687, 0.1517	0.0301, 0.0736	0.0675, 0.1642
R1, wR2 (all data)	0.1735, 0.2148	0.0426, 0.0833	0.1219, 0.2060
goodness of fit, F^2	1.006	1.049	1.013
no. data/restraints/params	of 8378/0/514	8457/0/514	4824/0/307
largest diff peaks, eÅ^{-3}	0.896 to –0.744	1.329 to –1.046	0.493 to –0.268

Table A.3. Selected Crystallographic Data for Compounds 94 and 95

	94	**95**
Formula	$C_{56}H_{64}Cl_2Ge_2P_2S_2$	$C_{50}H_{64}Cl_2O_2P_2S_2Zr$
Fw	1079.21	985.19
Color	Yellow	Yellow
cryst syst	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	10.996(3)	12.326(5)
b (Å)	23.065(7)	19.597(8)
c (Å)	21.156(6)	20.925(8)
α (deg)	90.00	90.00
β (deg)	99.443(6)	104.273(7)
γ (deg)	90.00	90.00
V (Å^3)	5293(3)	4898(3)
Z	4	4
d_{calcd} (g cm^{-3})	1.354	1.336
μ (mm^{-1})	1.412	0.522
F(000)	2240	2064
cryst size (mm)	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20
2θ range (deg)	1.32-25.00	1.45-25.00
index range	$-13 \le h \le 12$,	$-11 \le h \le 14$,
	$-23 \le k \le 27$,	$-22 \le k \le 23$,
	$-23 \le l \le 25$	$-24 \le l \le 24$
no. of rflns collected	28301	25704
no. of indep rflns	9299	8625
R1, wR2 ($I > 2(\sigma)I$)	0.0822, 0.2200	0.0695, 0.1547
R1, wR2 (all data)	0.1479, 0.2800	0.1610, 0.1970
goodness of fit, F^2	1.030	1.030
no. of data/restraints/params	9299/71/577	8625/15/550
largest diff peaks, eÅ^{-3}	2.906 to –0.680	0.620 to –0.331